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Properties of SbSI@CNTs and SbSI Nanowires

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Subjects presented[1] at DSL-2011:

- sonochemical preparation of
  antimony sulfoiodide (SbSI)-type nanowires,

- sonochemical filling of carbon nanotubes with SbSI
  (SbSI @ CNTs),

- ultrasonic welding of CNTs to metal electrodes.

[1] M. Nowak, K. Koziol, G. Kozlowski, J. Berdowski, J. Kasperczyk, I. Kityk, K. Mistewicz, M. Jesionek, **Ultrasonics and Carbon Nanotubes ,** Special Session**:** Carbon and Oxide Based Nanostructured Materials at the 7th Internat. Conf. DSL-2011, Algarve, Portugal.

Properties of SbSI

- **semiconductor** (**E_{glf} = 1.83(3) *eV***)

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- low coercive field E_c=10^4 V/m (T=0^{o}C, 50 Hz)
- high electromechanical coupling (k_{33}=0.9)

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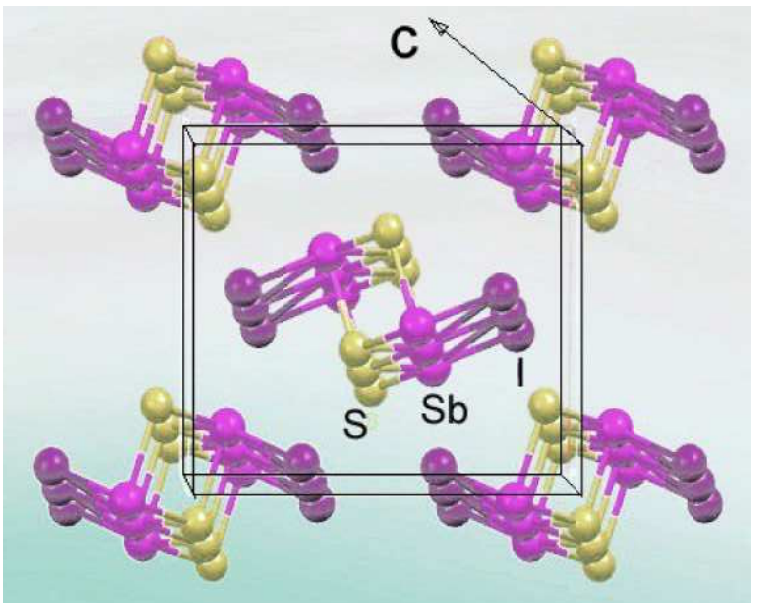
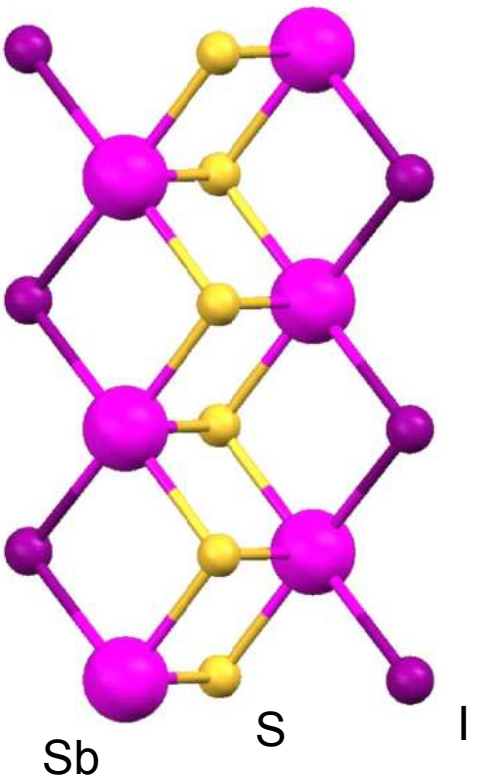
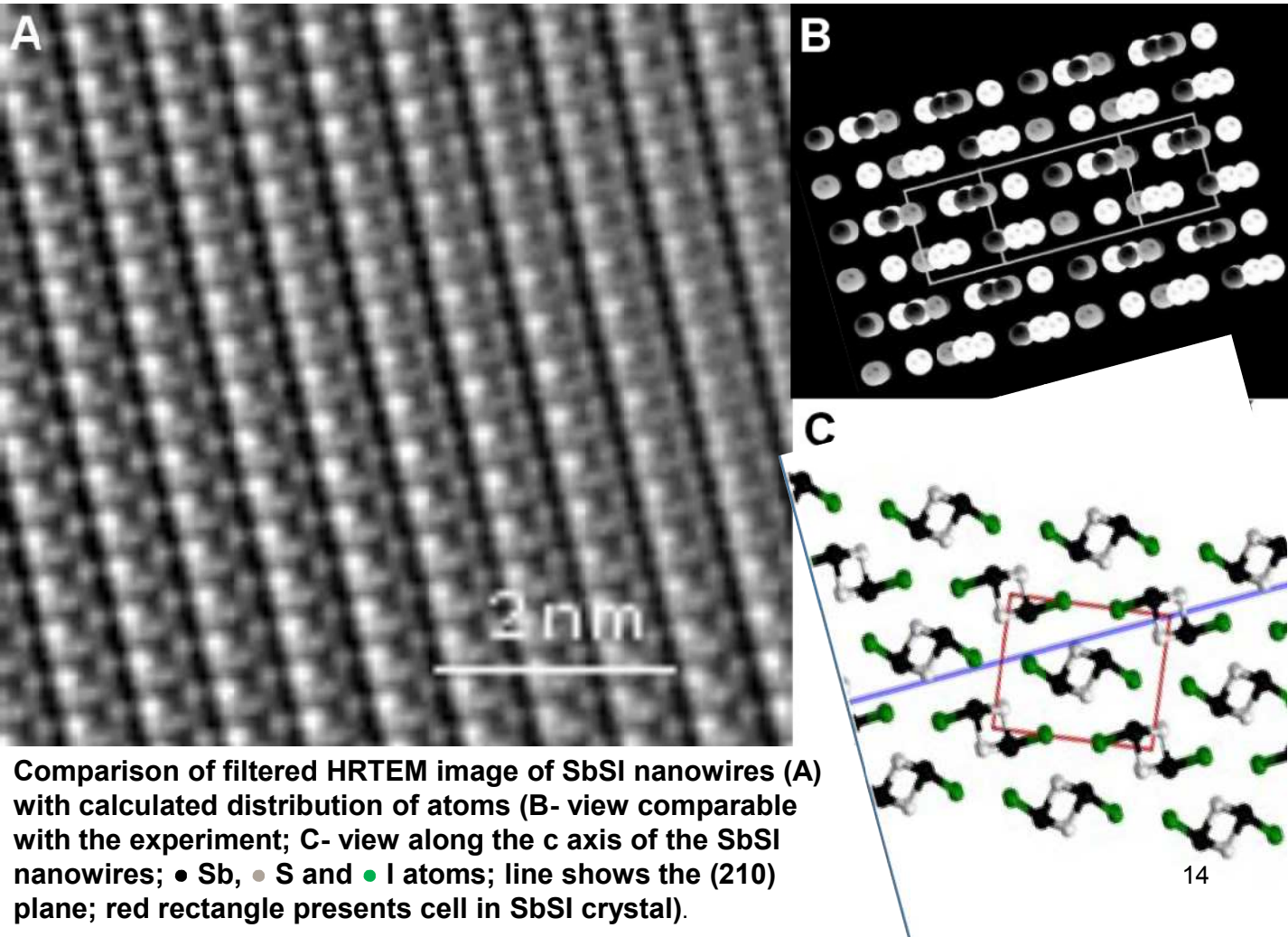


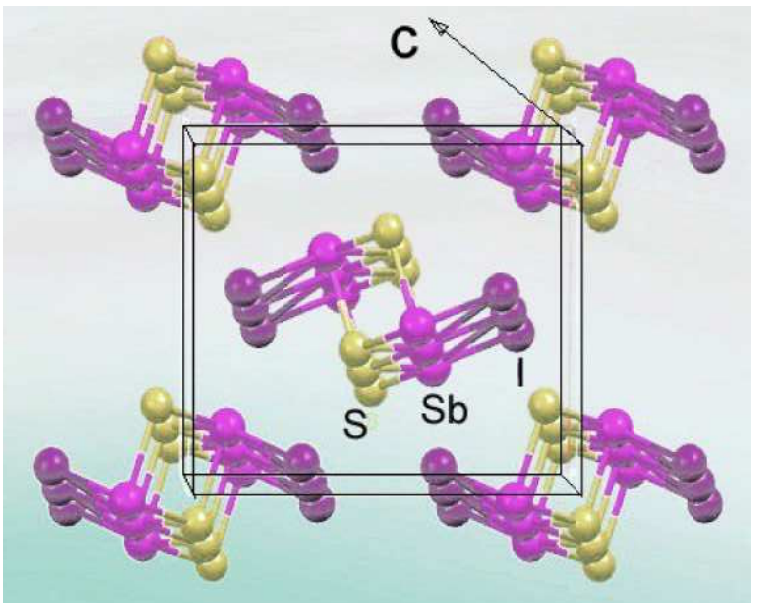


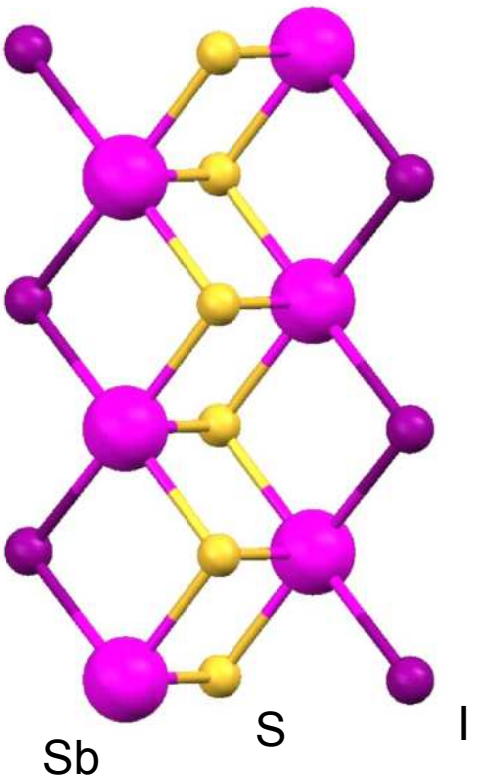
a = 0.853 nm, *b* = *1.017 nm,*
c = 0.408 nm



Comparison of filtered HRTEM image of SbSI nanowires (A) with calculated distribution of atoms (B- view comparable with the experiment; C- view along the c axis of the SbSI nanowires; ● Sb, ● S and ● I atoms; line shows the (210) plane; red rectangle presents cell in SbSI crystal).

- strong anisotropy





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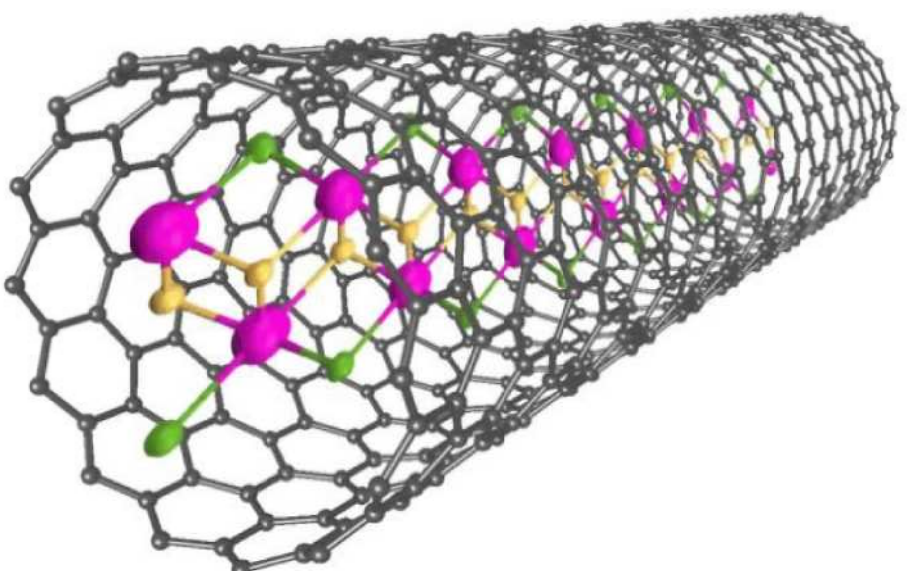
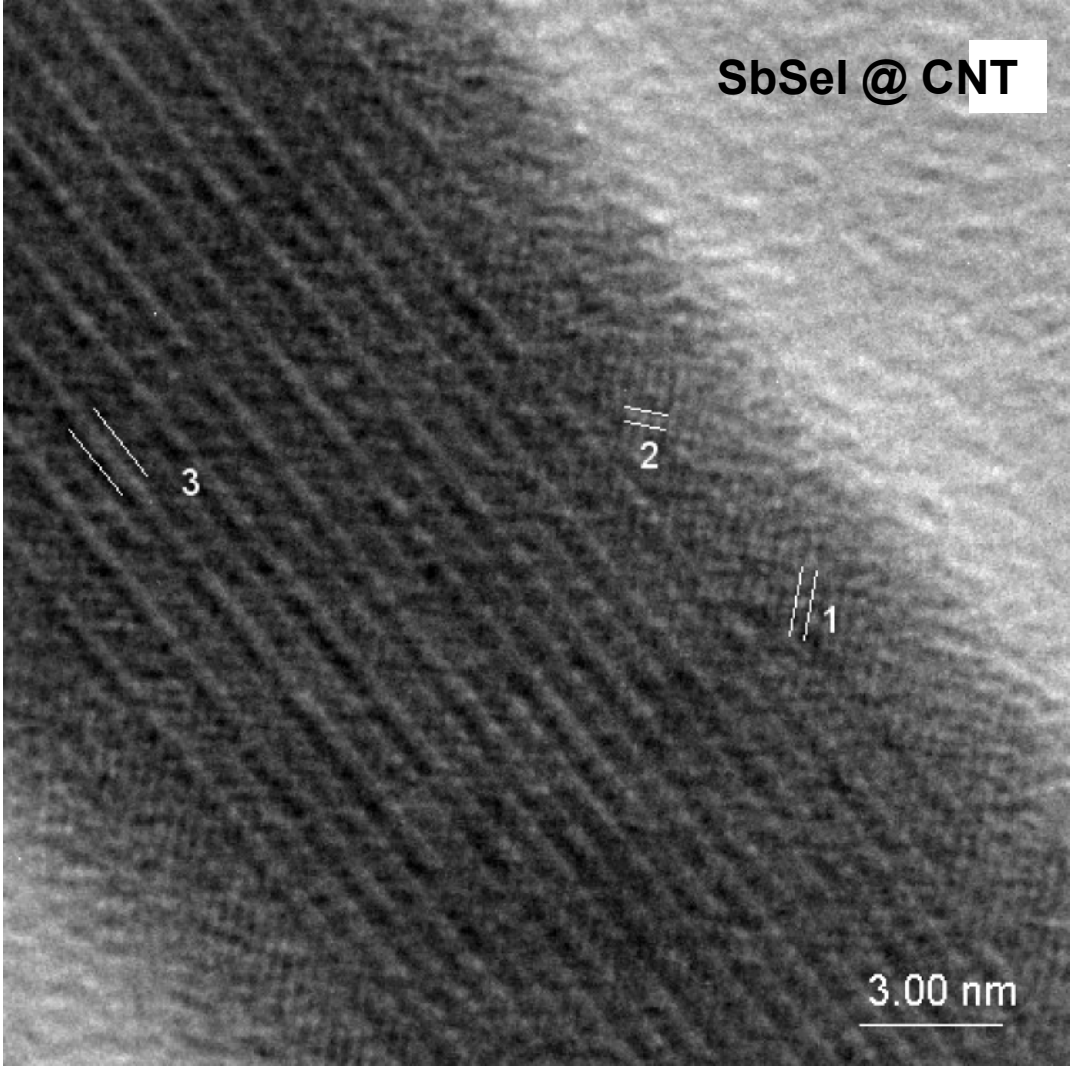
SbSI @ CNTs

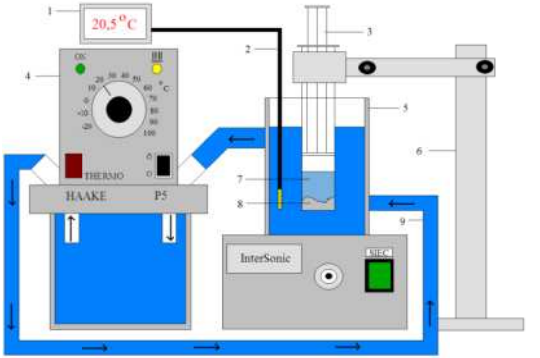
SbSeI @ CNTs




SbSeI @ CNT
3
2
1
3.00 nm

The **sonochemical technique** based on **cavitation** is :

- convenient,
- fast,
- efficient technique of nanotechnology.



Befor and after sonochemical synthesis of SbSI in ethanol

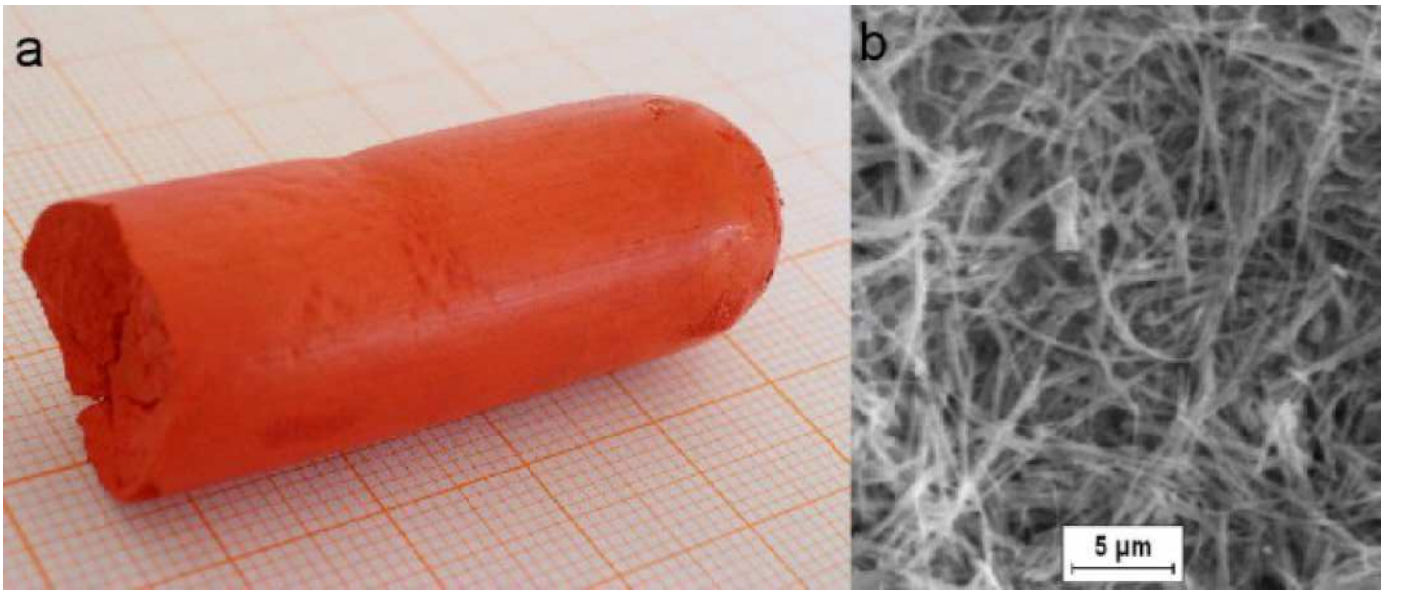
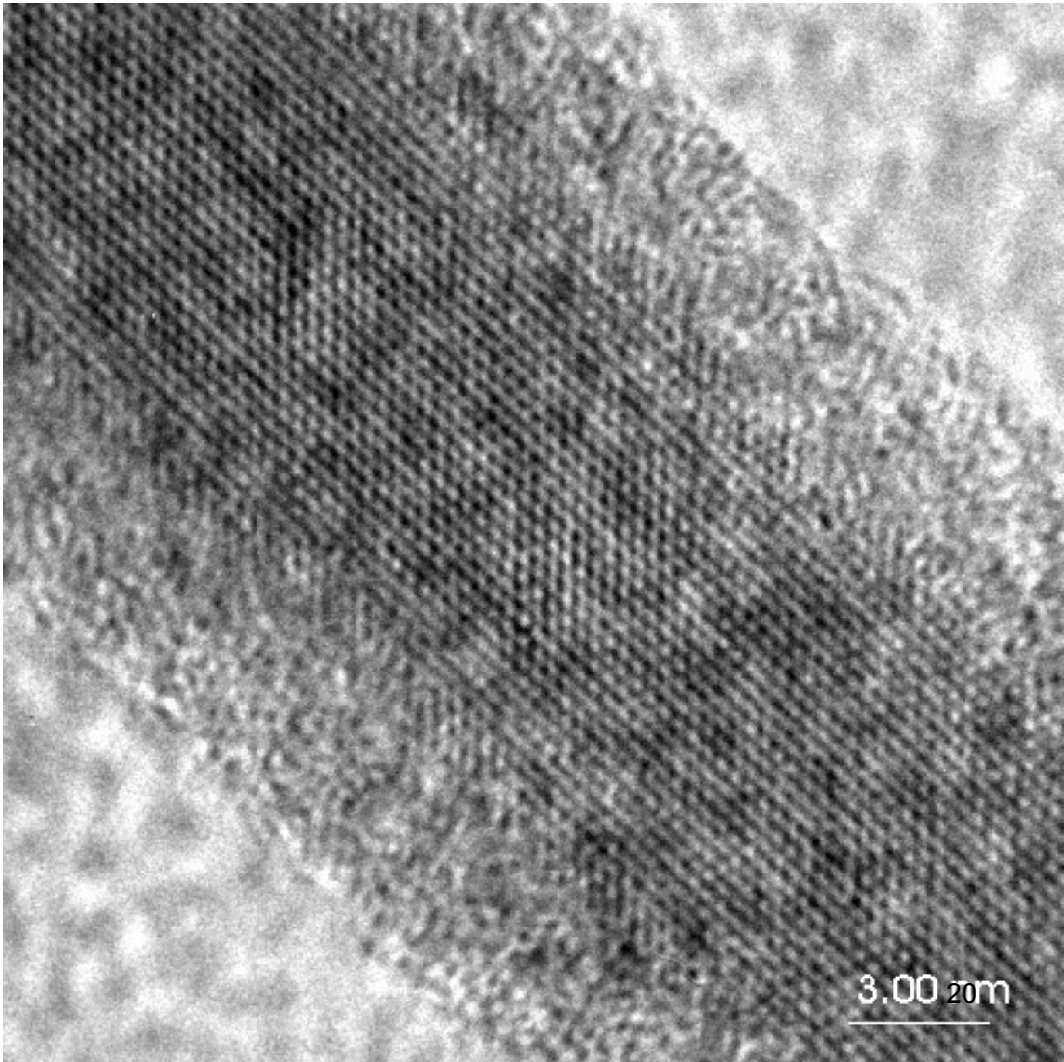
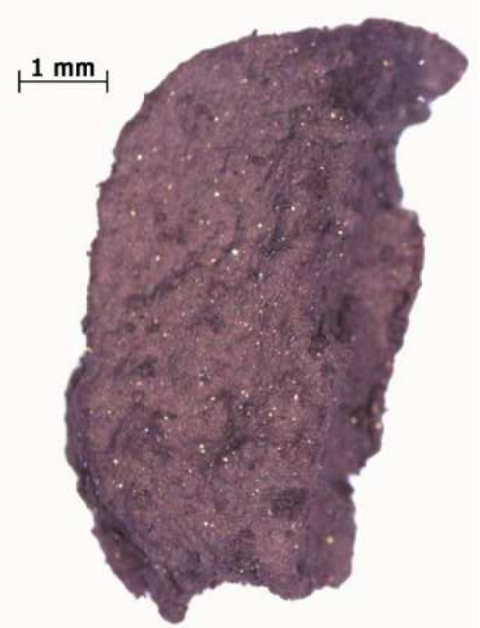


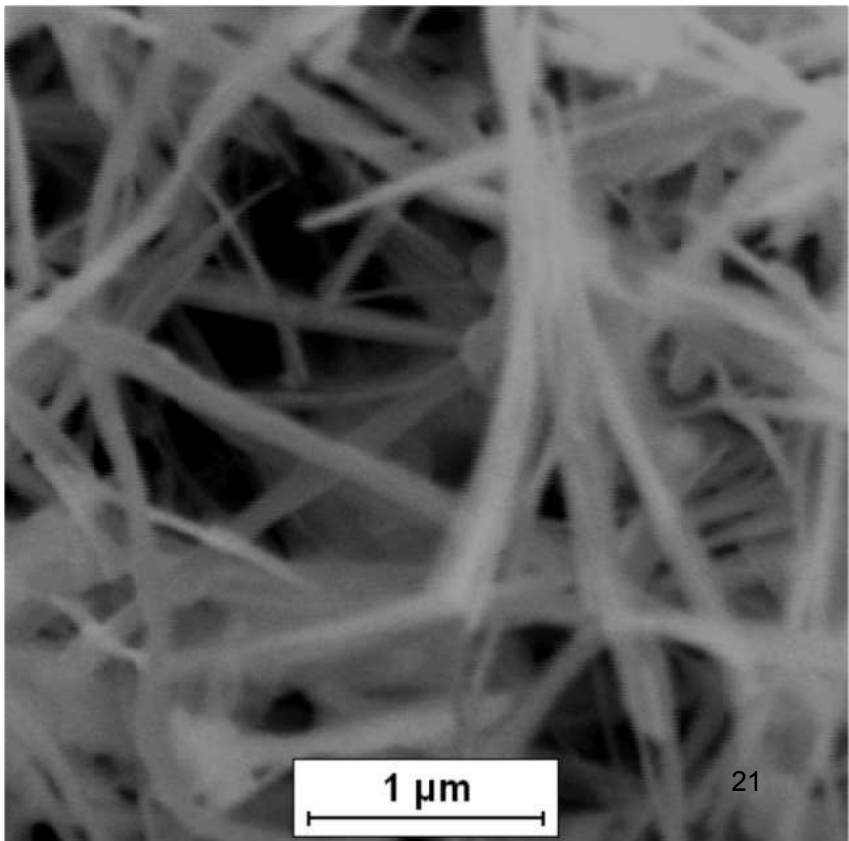
Image (a) and typical SEM micrograph (b) of sonochemically prepared SbSI gel.

HRTEM image of individual nanowire of SbSI

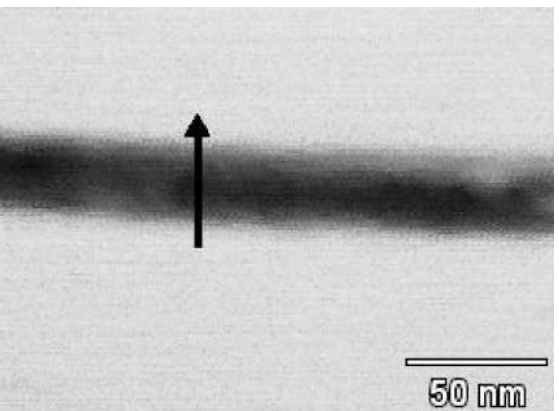


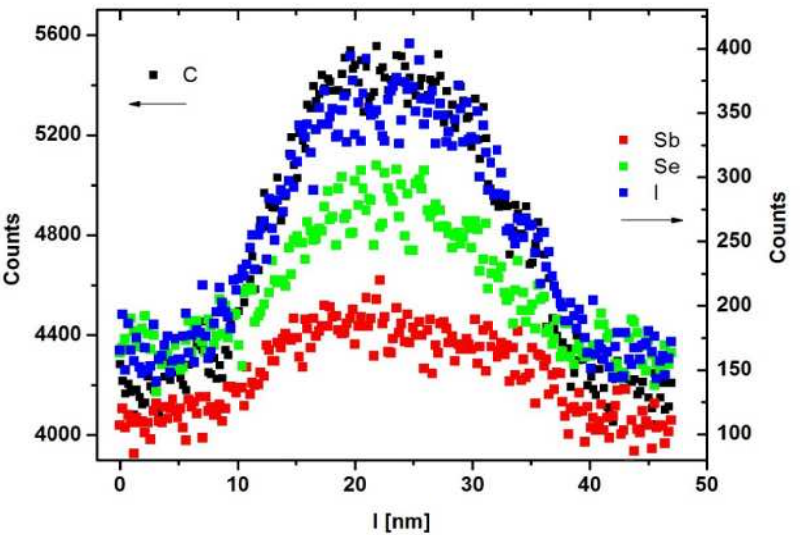


Dried multiwalled CNTs filled with SbSI sonochemically in methanol.



Typical SEM micrograph of dried multiwalled CNTs filled with SbSI sonochemically in methanol.





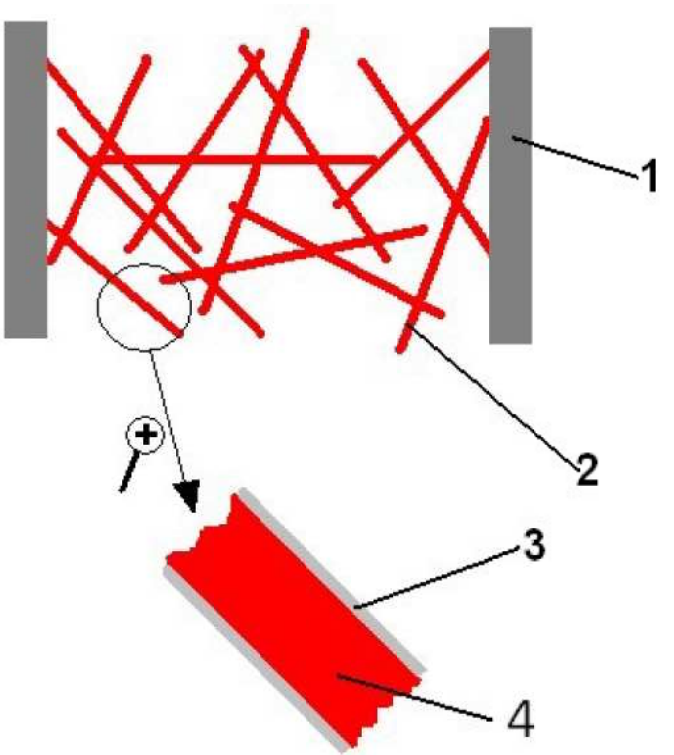
TEM line scan EDS for SbSeI encapsulated in CNT

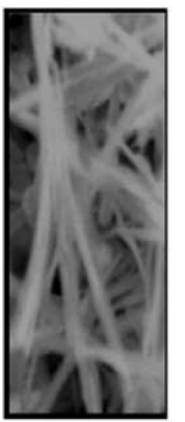
New subject:

sensing properties

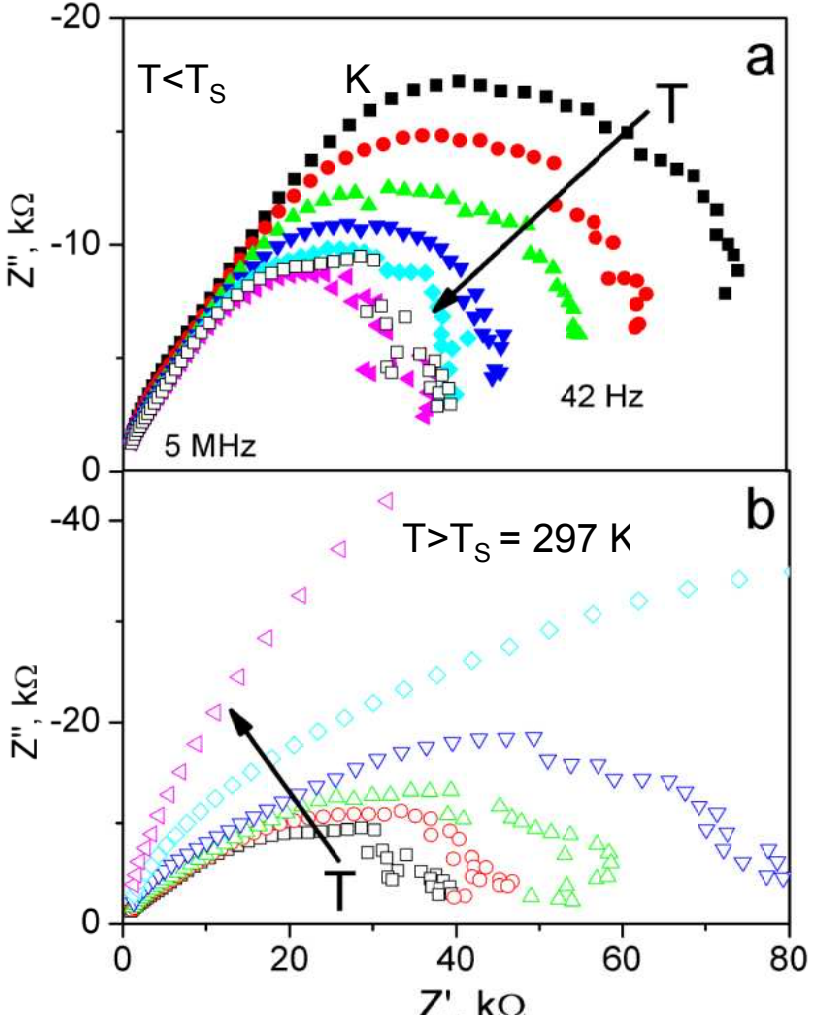
of SbSI @ CNTs and SbSI nanowires

Electrical investigations of no welded SbSI@CNTs or SbSI nanowires





1- electrodes,
2- SbSI@CNTs or SbSI nanowire,
3- CNT or surface layer,
4- SbSI nanowire.

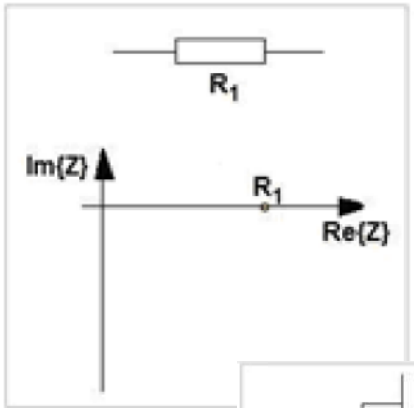


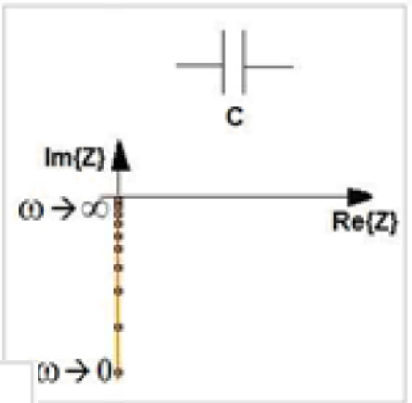
Influence of temperature and humidity on Nyquist plots of SbSI gel

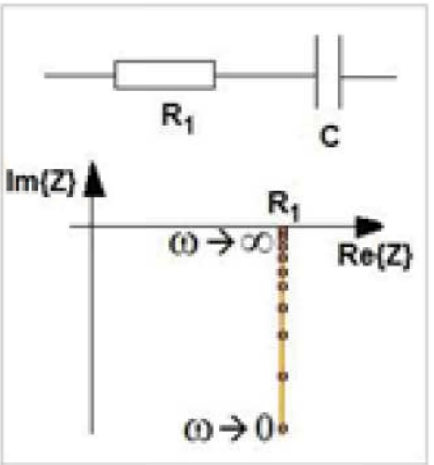
- T=289 K, RH= 87 %;
- T=291 K, RH= 86 %;
- T=293 K, RH= 85 %;
- T=295 K, RH= 84 %;
- T=297 K, RH= 84 %;
- T=299 K, RH= 83 %;
- T=300 K, RH= 80 %;
- T=302 K, RH= 57 %;
- T=304 K, RH= 45 %;
- T=306 K, RH= 41 %;
- T=308 K, RH= 36 %;
- T=310 K, RH= 34 %;

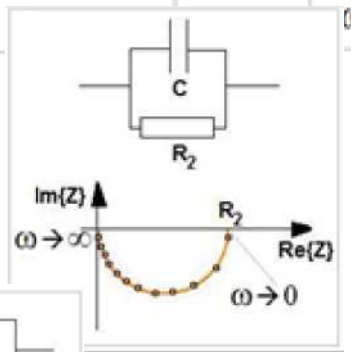
E = 290 V/m, p = 1 atm).

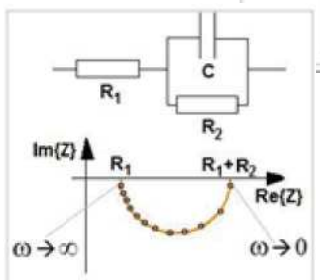
Impedance spectroscopy

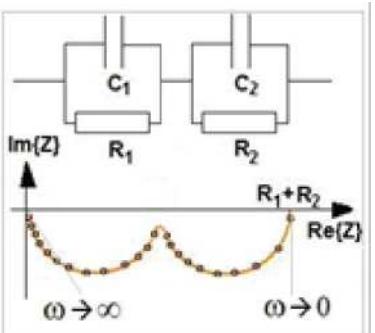


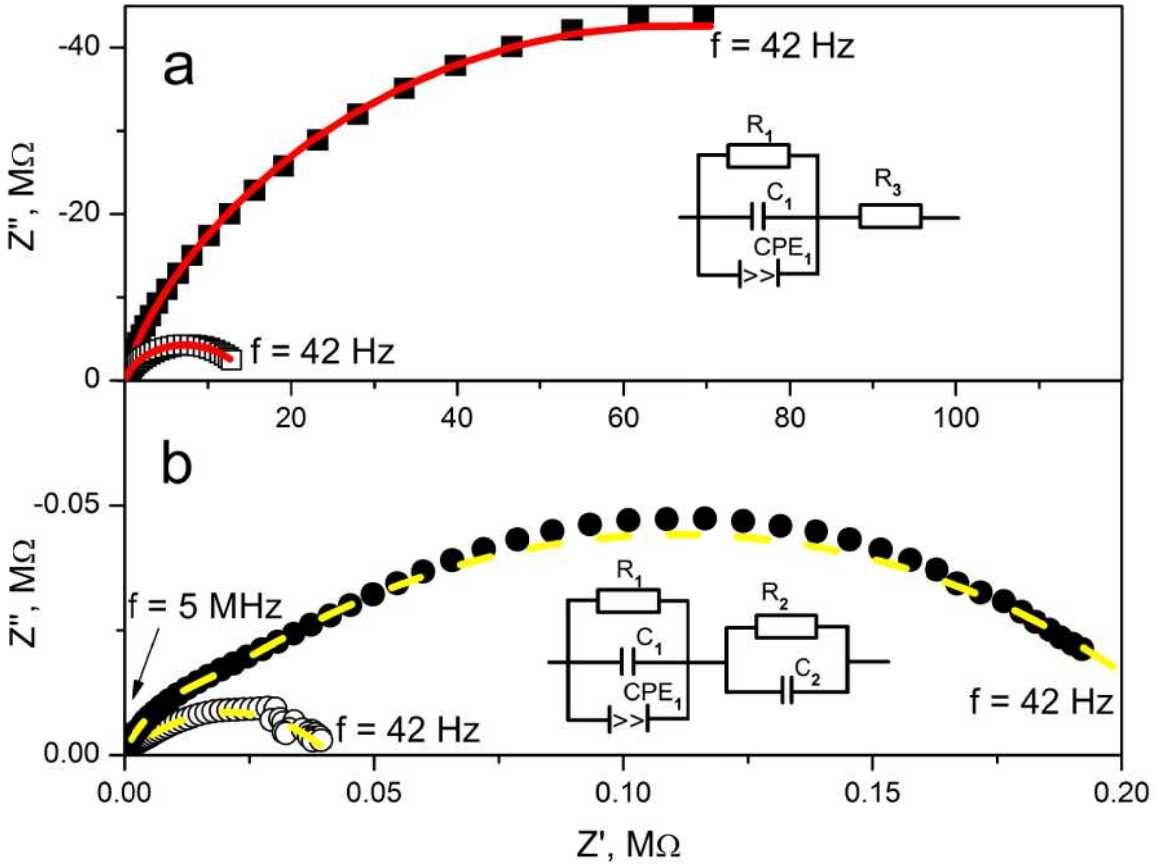








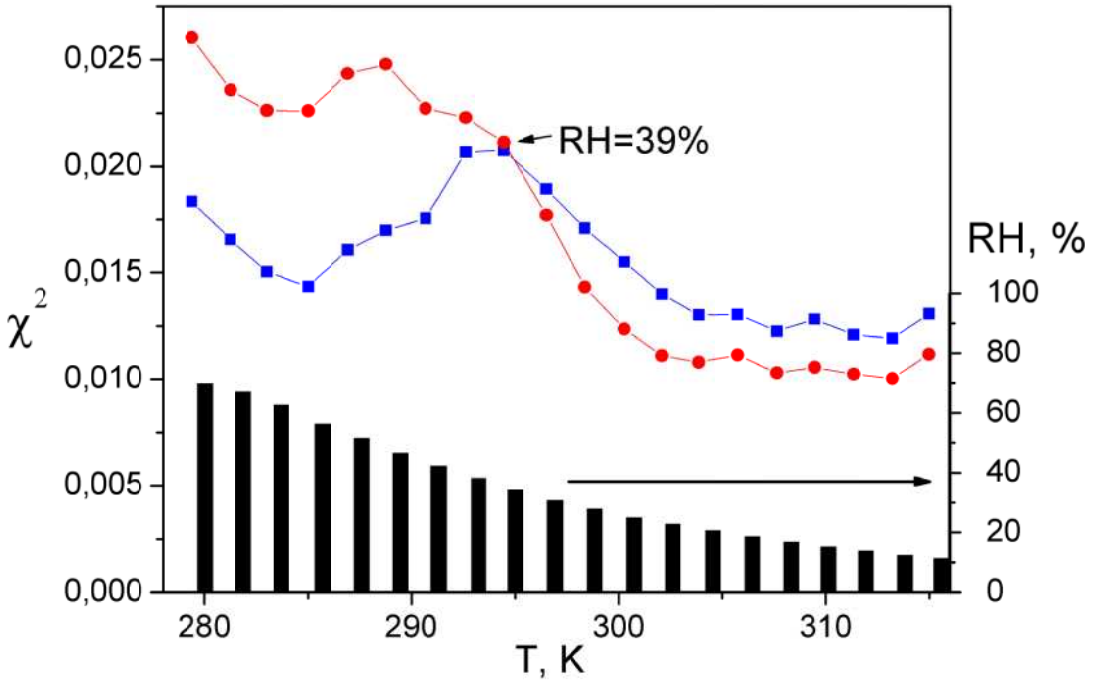




RH=20 %

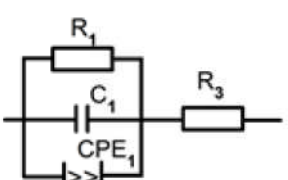
RH=80 %

Influence of temperature on Nyquist plot for SbSI gel for constant humidity (■ – T=281 K; □ – T=304 K; ● – T=281 K; ○ – T=300 K).

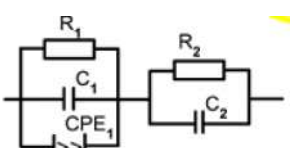


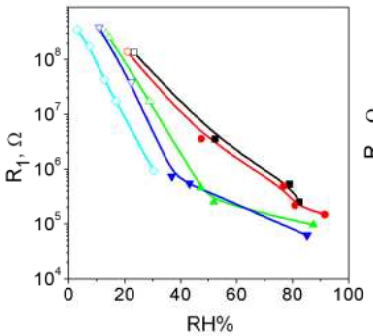
Sum of the least squares obtained when data registered under different ambient conditions of SbSI gel (black bars) were fitted with different models

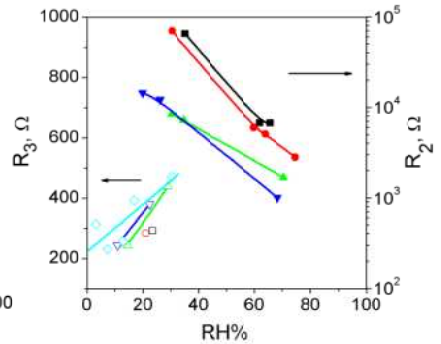
● **for**

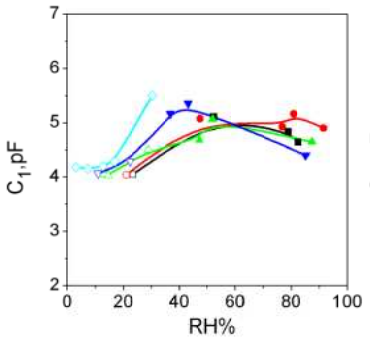


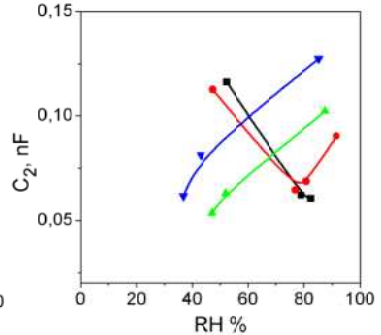
■ **for**

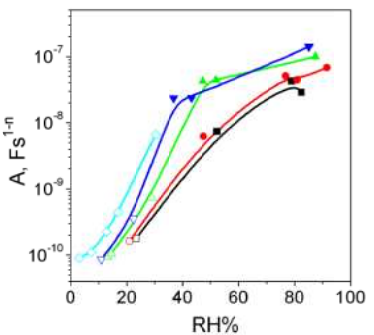


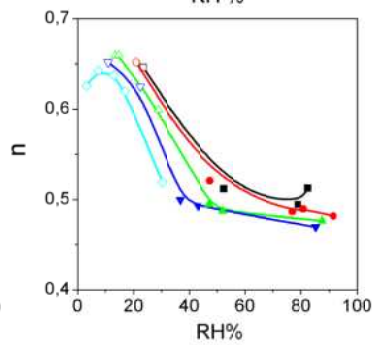








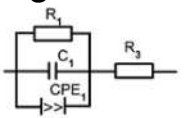




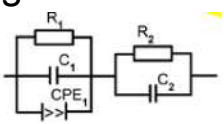
Influence of humidity on resistance and capacitance parameters of equivalent circuits used to interpret Nyquist plots for different temperatures

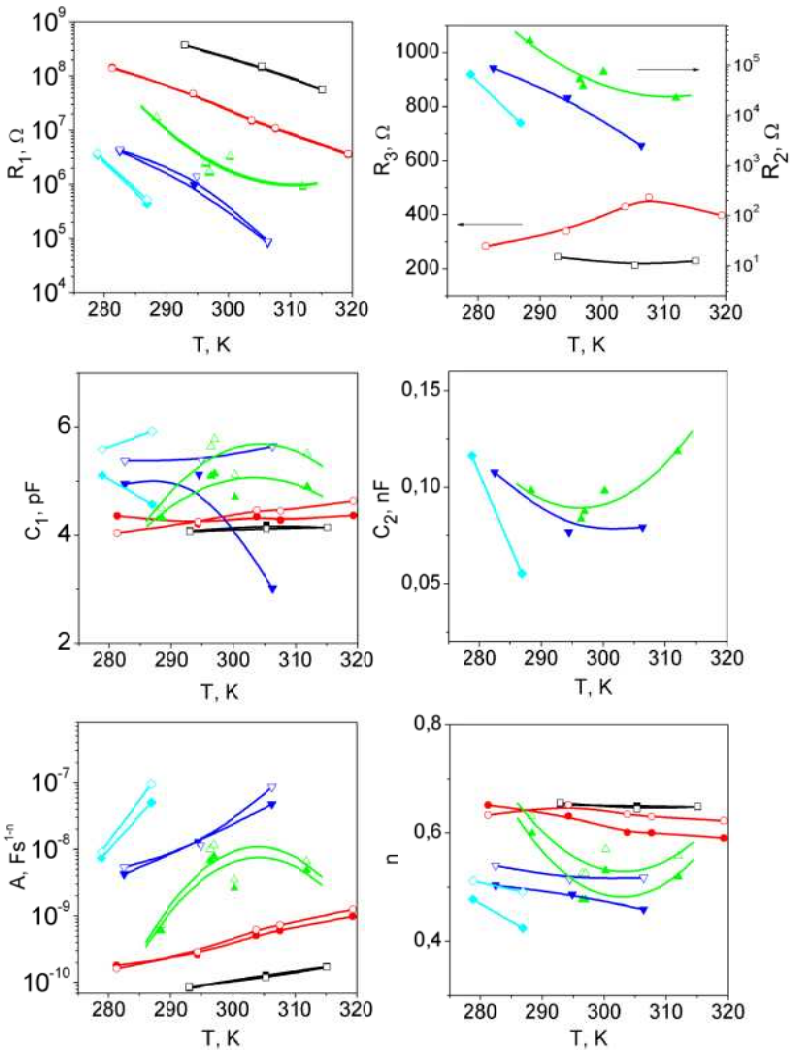
- ■ - RH= 10 %;
- ● - RH= 20 %;
- ▲ - RH= 30 %;
- ▼ - RH= 40 %;
- ♦ - RH= 55 %)

open signs – model:



full signs – model:





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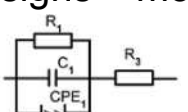
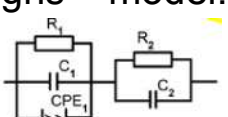
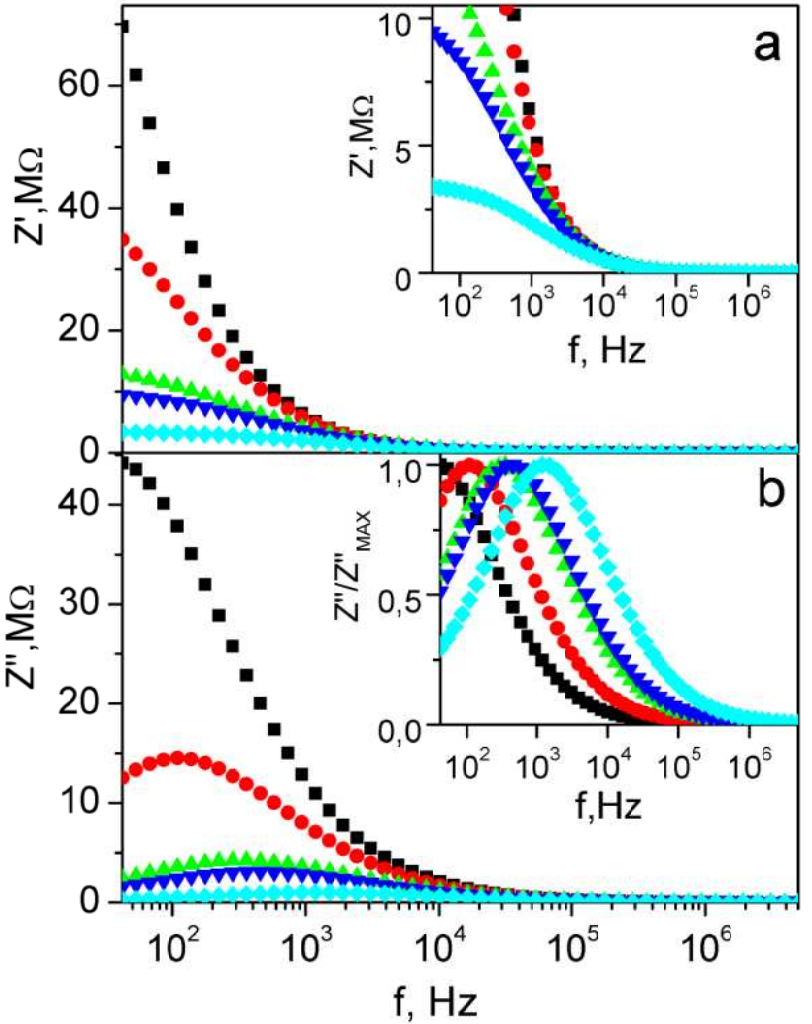


full signs – model:

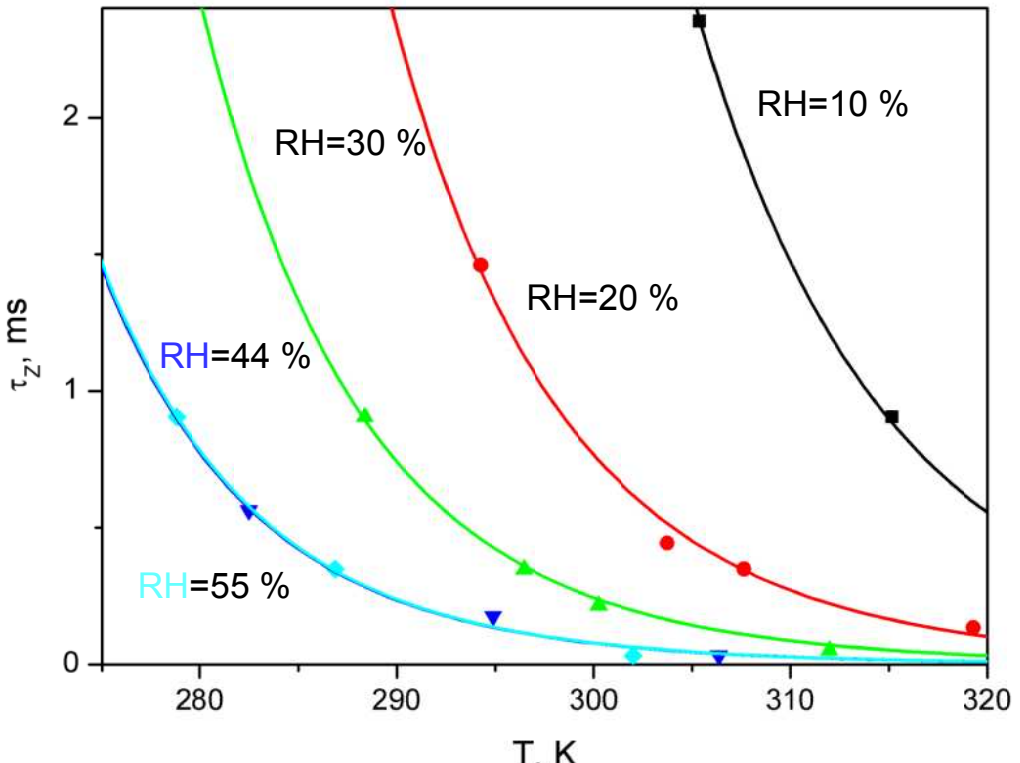




Influence of temperature on frequency response of real (a) and imaginary (b) parts of impedance of SbSI gel for constant humidity:

- ■ - T=281 K; RH=20 %
- ● - T=294 K; RH=20 %
- ▲ - T=304 K; RH=20 %
- ▼ - T=307 K; RH=20 %
- ♦ - T=319 K; RH=20 %

$$2\pi f_{MAX}\,\tau_Z = 1$$

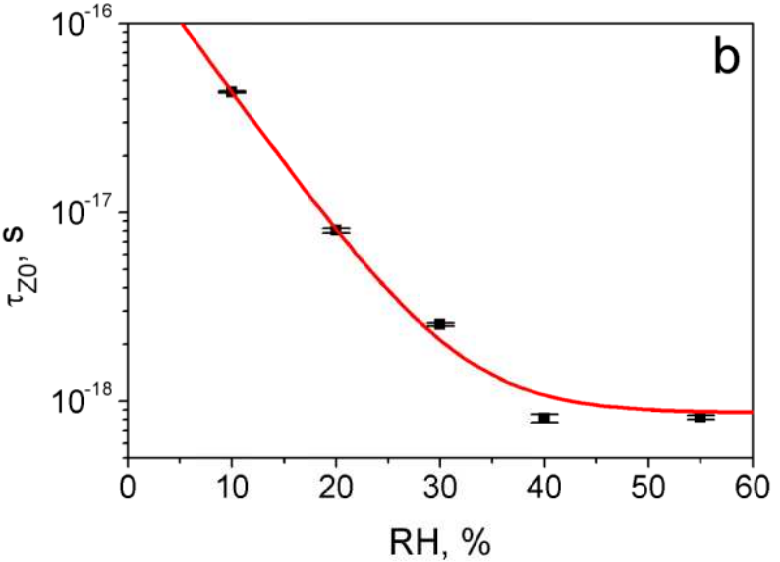


Influence of temperature and humidity on relaxation time of SbSI gel

$$\tau_Z = \tau_{Z0} \exp\left(\frac{E_a}{k_B T}\right)$$

E_a=(0.832 ± 0.067) eV [32]

$$\tau_Z = \tau_{Z0} \exp\left(\frac{E_a}{k_B T}\right)$$

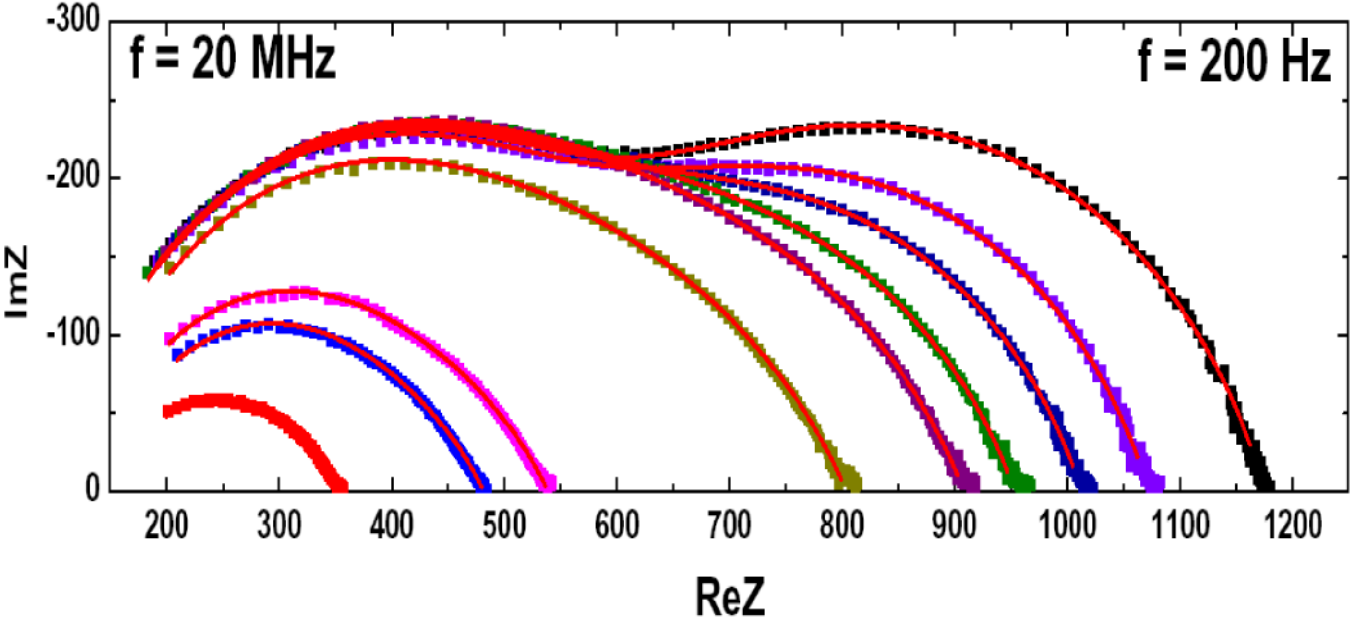


Influence of humidity on pre-exponential factor describing temperature dependence of relaxation time of SbSI gel

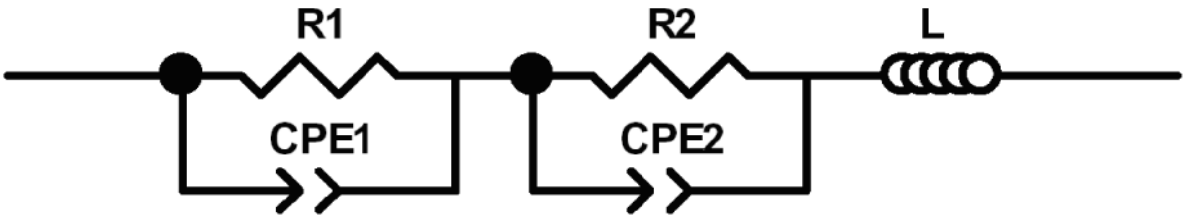
$$\tau_{Z0}(RH) = \tau_{Z0}(RH = 0) \exp\left(\frac{-RH}{B}\right) + \tau_{ZRH\,max}$$

$t_{Z0}(RH=0)=(2.49\pm \cdot {}^{-16}$ s, $B=5.7\pm 0.2$, $t_{ZRHmax}=(0.87\pm \cdot {}^{-18}_{33}$ s

SbSI @ CNTs



Influence of temperature on Nyquista plots for CNTs filled with SbSI (■ – 273 K, ■ – 283 K, ■ – 293 K, ■ – 303 K, ■ – 313 K, ■ – 323 K, ■ – 333 K, ■ – 343 K, ■ – 353 K). Solid curves represent the fitted theoretical dependences calculated for an equivalent circuit.

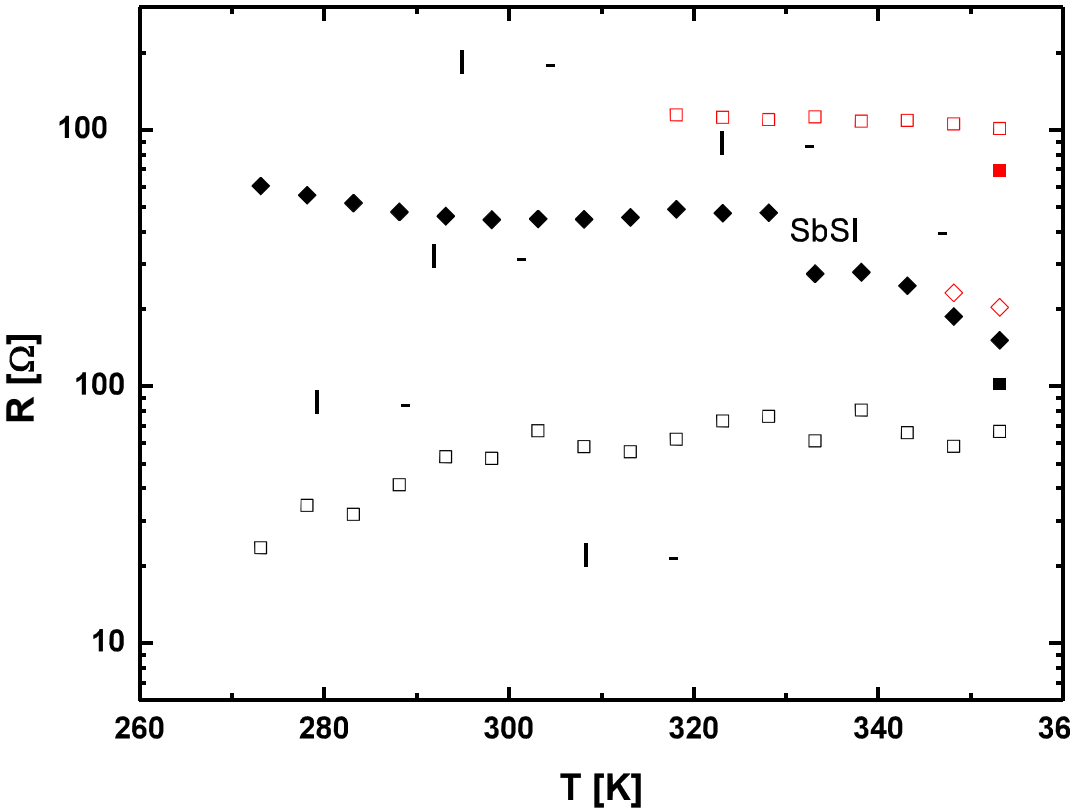


Equivalent circuit describing Nyquist plot of SbSI@CNT sonochemically prepared in methanol

Impedance of → constant phase element (CPE)

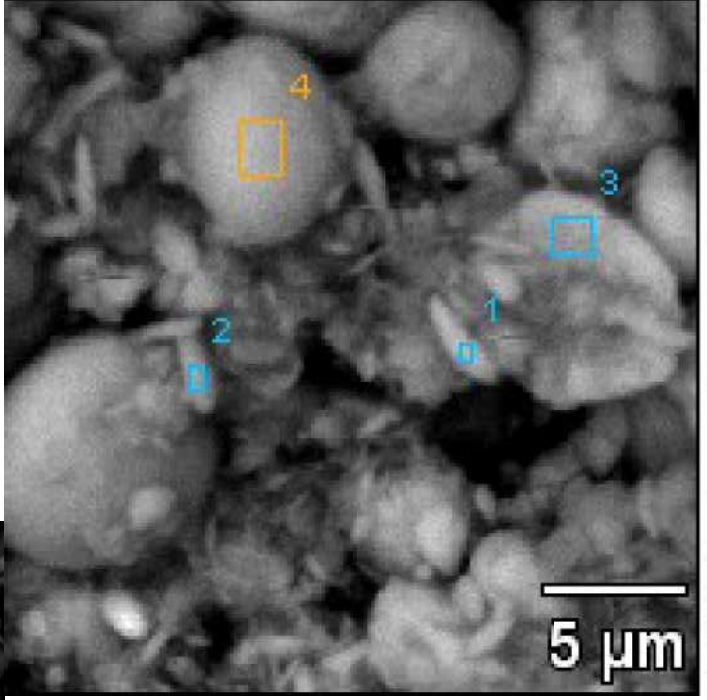
$$Z_{CPE} = \left[A(j\omega)^n\right]^{-1}$$

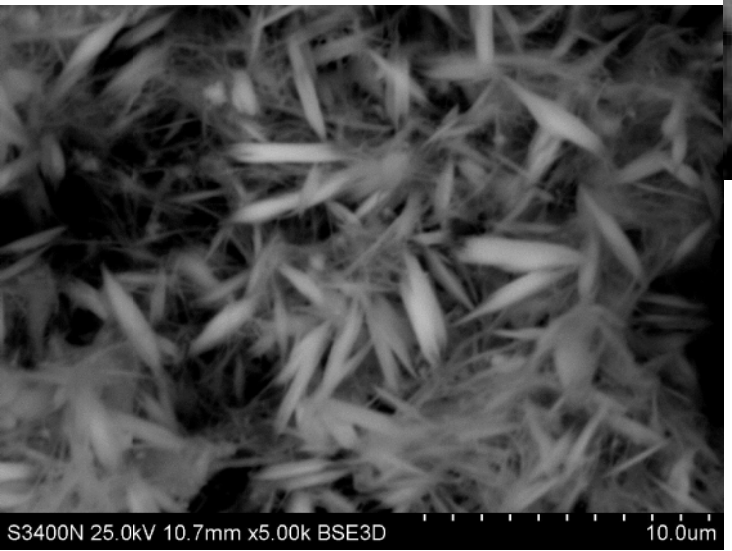
n = 1 for ideal capacitor and n = 0 for ideal resistor



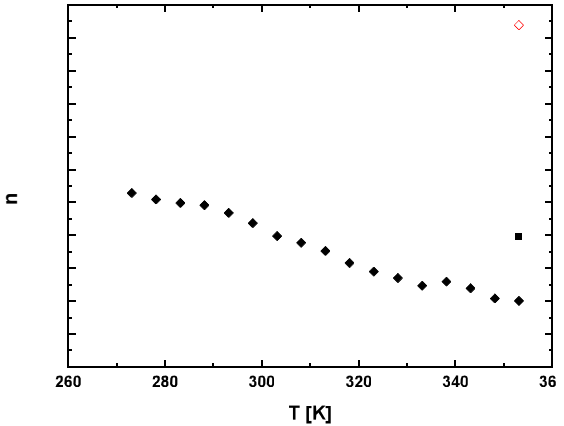
Comparison of the temperature dependences of resistance parameters of equivalent circuits describing Nyquist plots registered in the cases of SbSI@CNT sonochemically prepared in methanol (◇ – R_1, ◆ – R_2), and SbSI@CNT (■ – R_1, ■ – R_2) and SbSeI@CNT (□– R_1, □ – R_2) ultrasonically prepared in ethanol.

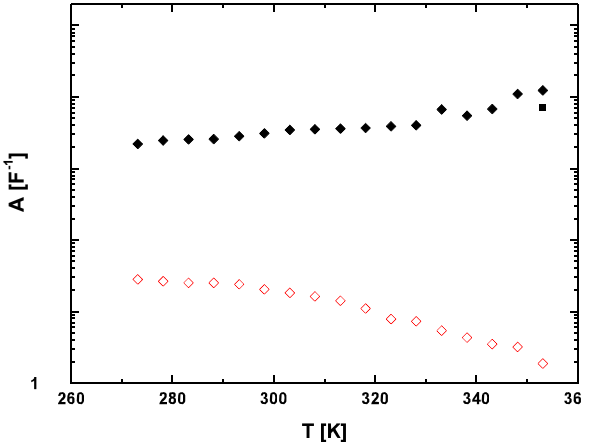
SbSI after 30 min. of sonochemical synthesis in toluene

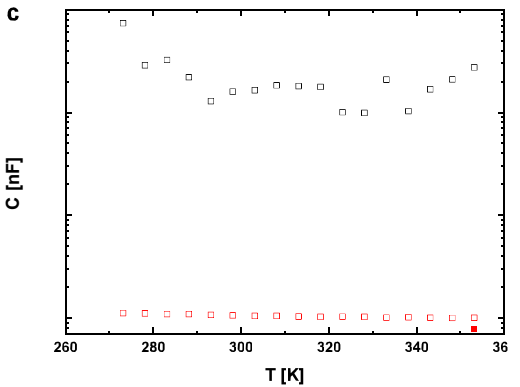




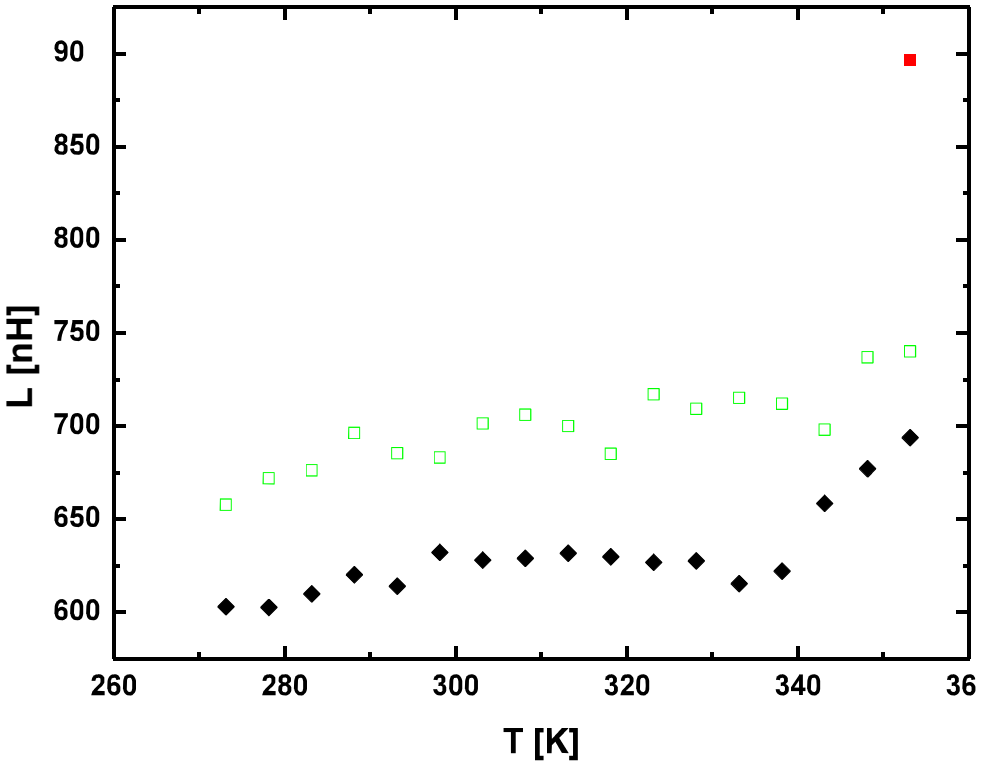
SbSI after 120 min. of sonochemical synthesis in toluene



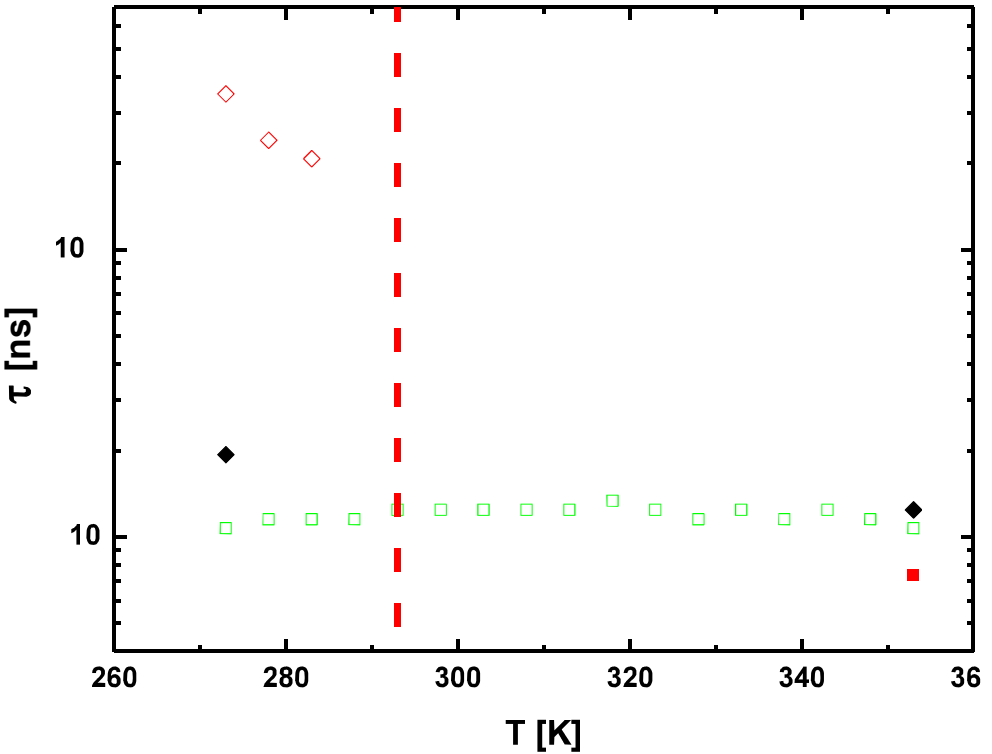




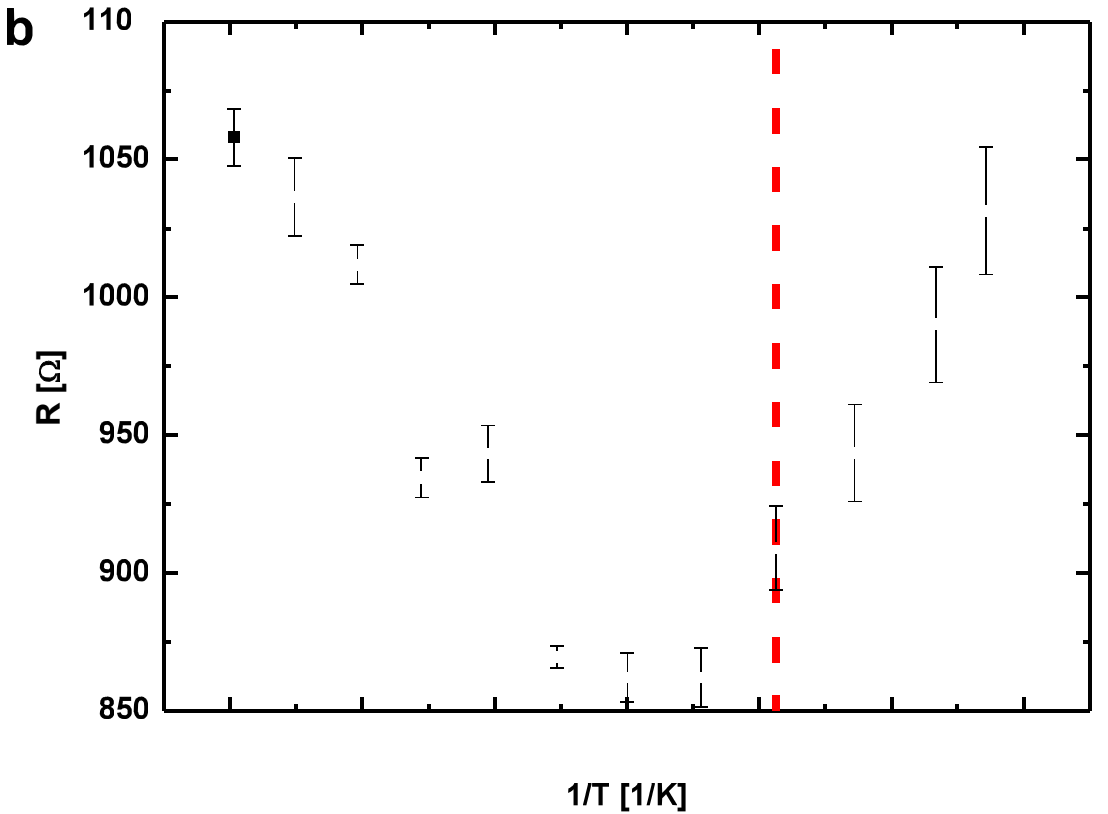
Comparison of capacitance parameters of equivalent circuits describing Nyquist plots of SbSI@CNT sonochemically prepared in methanol (◆– n_1, A_1; ◇ – n_2, A_2), and SbSI@CNT (■ – n, A; ■ – C) and SbSeI@CNT (□ – C_1, □ – C_2) sonochemically prepared in ethanol.



Comparison of inductance parameters of equivalent circuits describing Nyquist plots of SbSI@CNT sonochemically prepared in methanol (◆), and SbSI@CNT (■) and SbSeI@CNT (□) ultrasonically prepared in ethanol

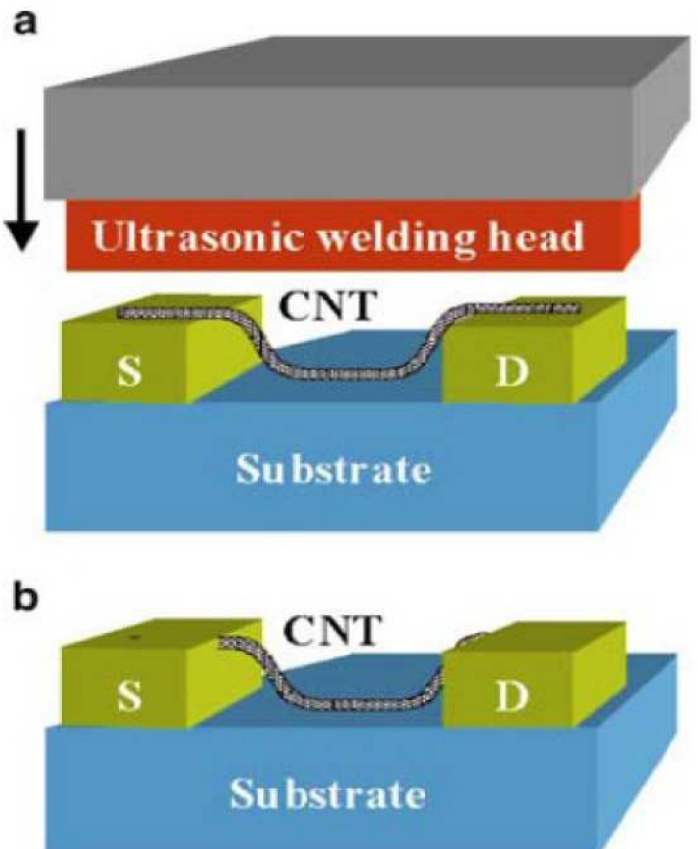


Comparison of the temperature dependences of relaxation time of SbSI@CNT sonochemically prepared in methanol (◆ – t_1, ◇ – t_2), and SbSI@CNT (■) and SbSeI@CNT (□) ultrasonically prepared in ethanol.[40]



Temperature dependence of SbSI @ CNT d.c. resistance

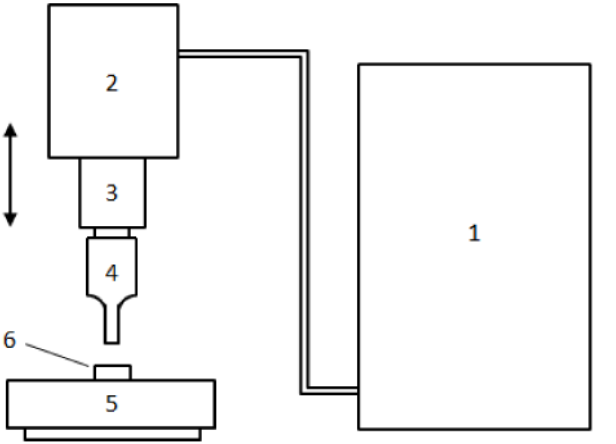
(p= · $^{-3}$ mbar; vertical line represents T_c = 293 K for bulk crystals)



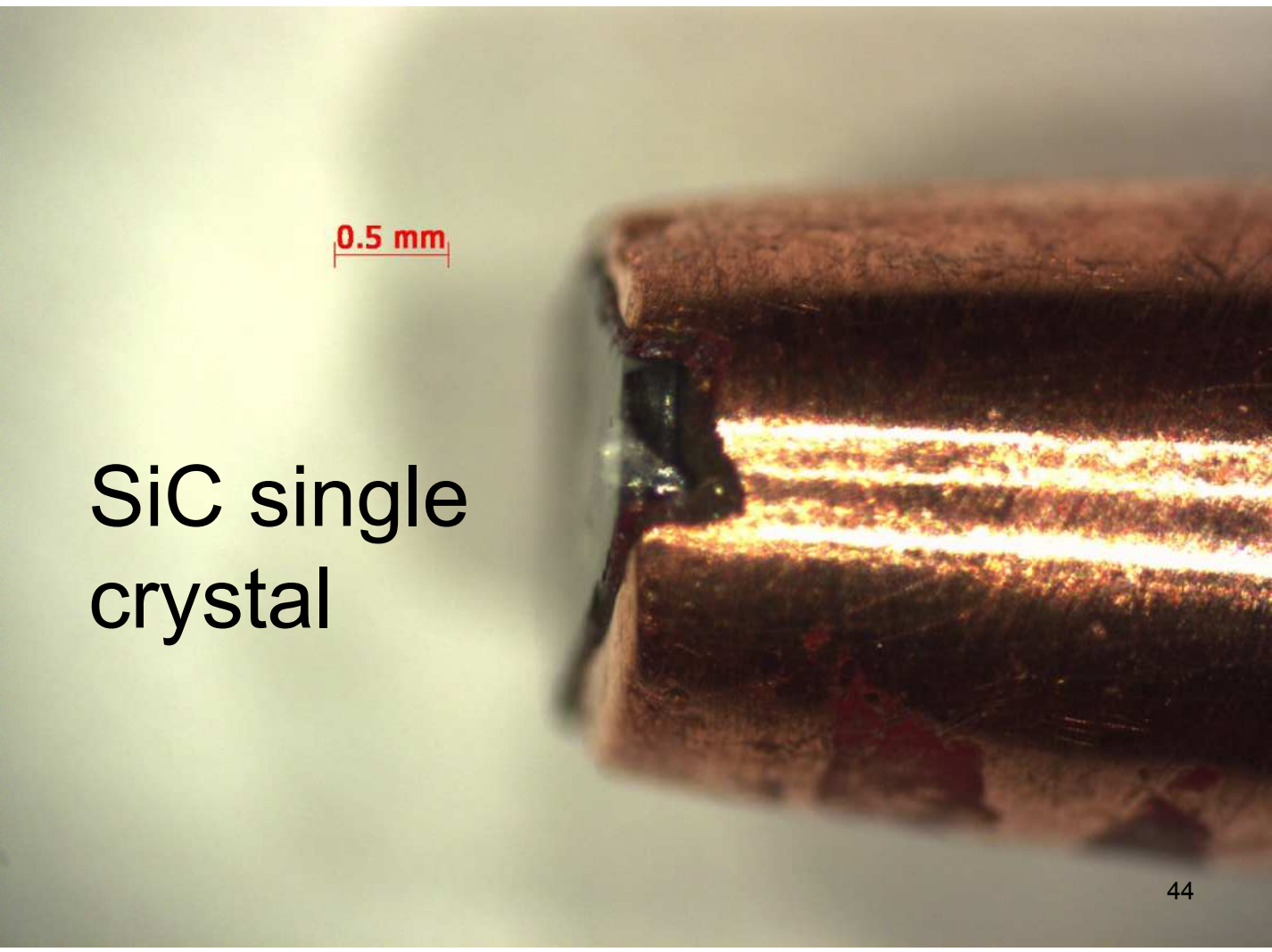
Al_2O_3 single crystal

Ultrasonic nanowelding

1 - ultrasonic generator 70 kHz
ADG70-100P-230-NO
(Rinco Ultrasonics)
3 - transducer C 70-2
(Rinco Ultrasonics)
5 - digital scale



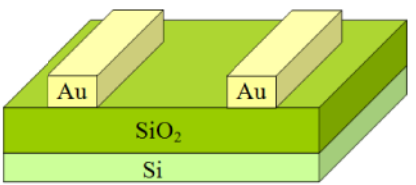
2 - holder
4 - special sonotrode made by myself
(surface roughness - order of magnitude nm)
6 - sample

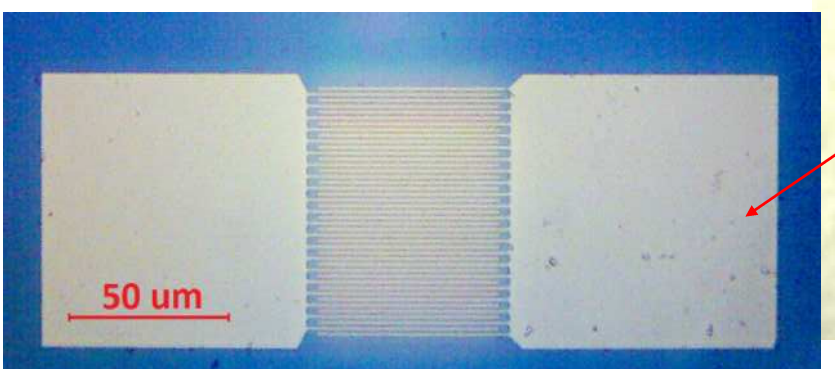


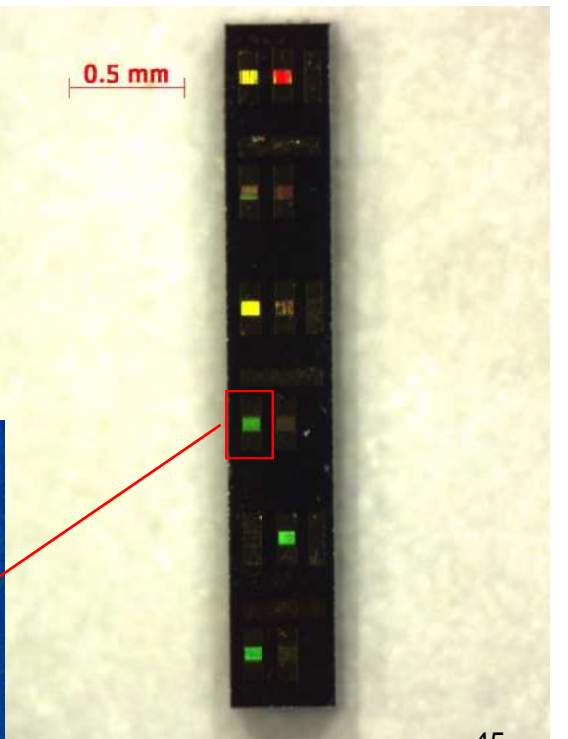
SiC single crystal

Si/SiO_2 substrates

made by:
Wroclaw University of Technology;
electrode spacing: 0.6, 1.2 or 2.5 μm

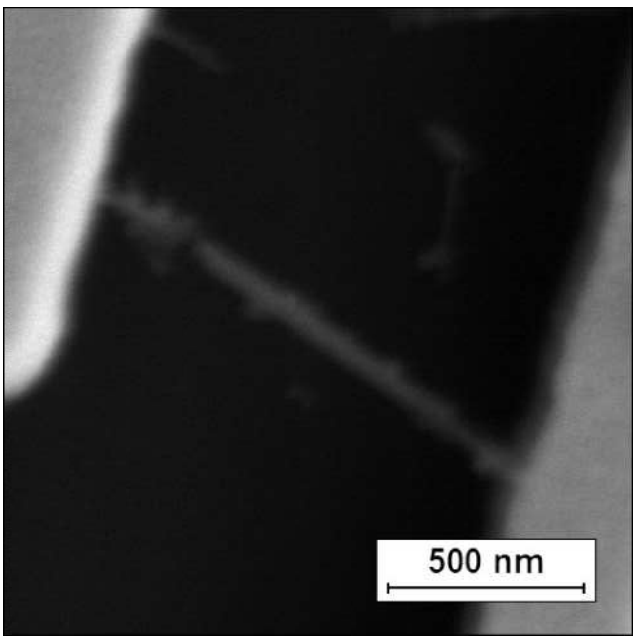


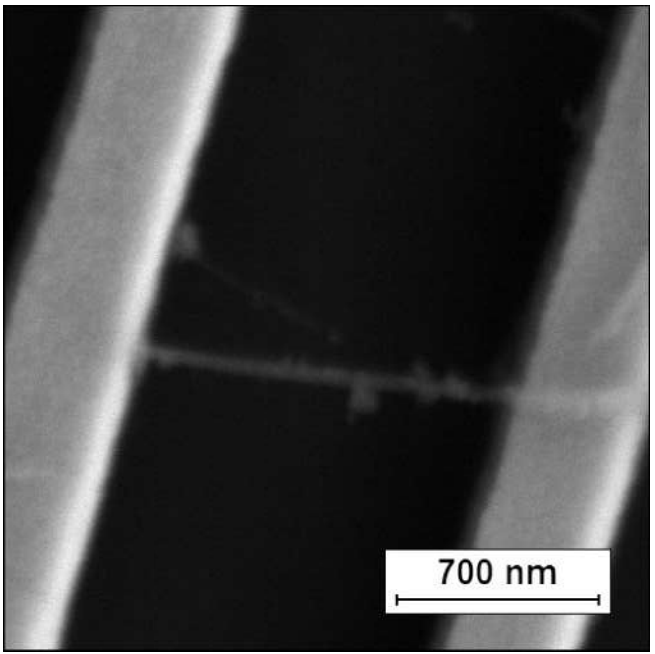


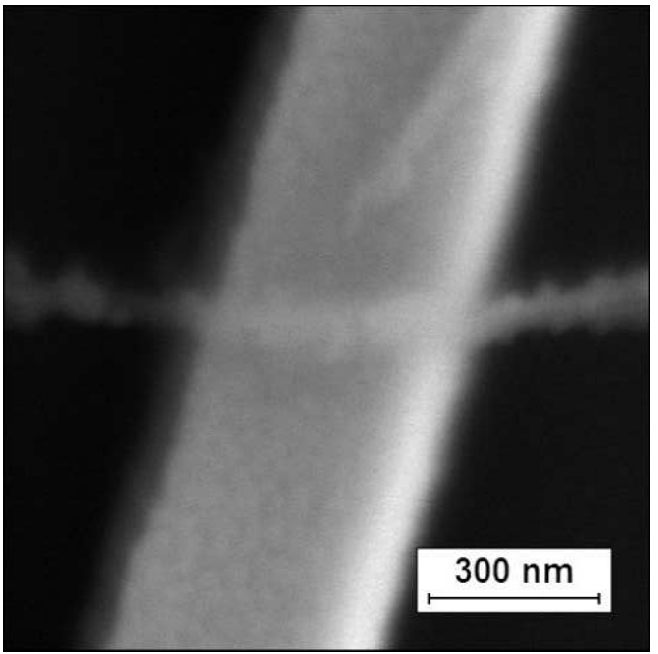


Alignment in electric field

- SbSI nanowires ultrasonically agitated in toluene ($C_6H_5CH_3$)
- applied electric field E = · ^{5} V/m

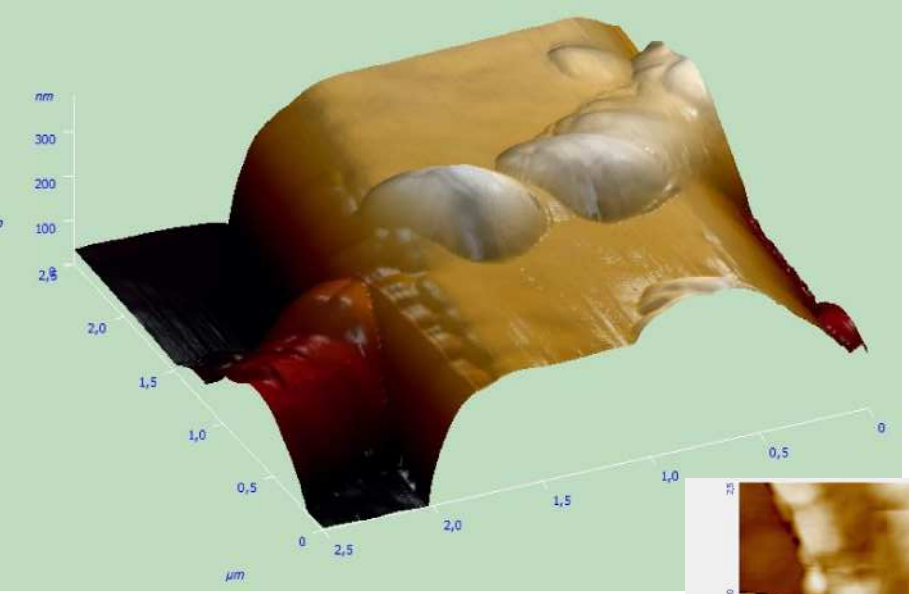




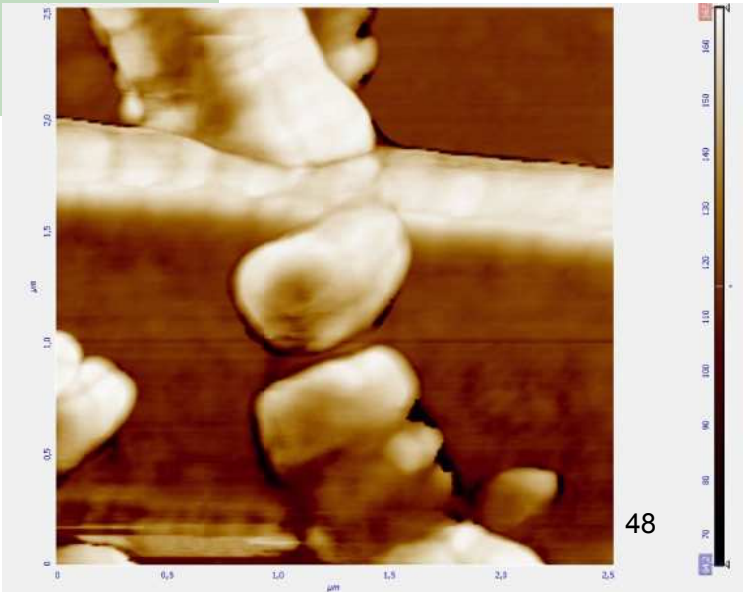


SbSI nanowires on Si/SiO_2 substrate

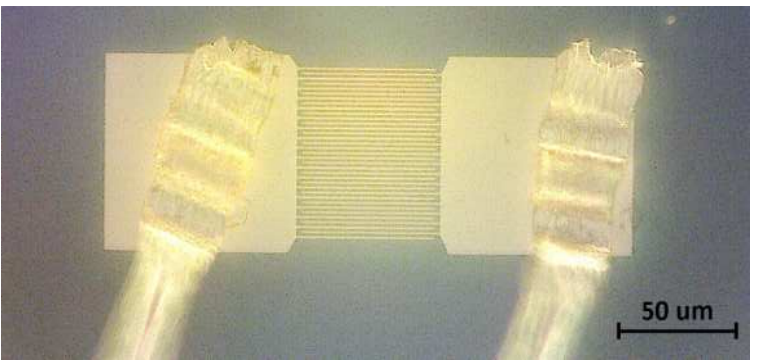
with Au electrodes after ultrasonic nanowelding.

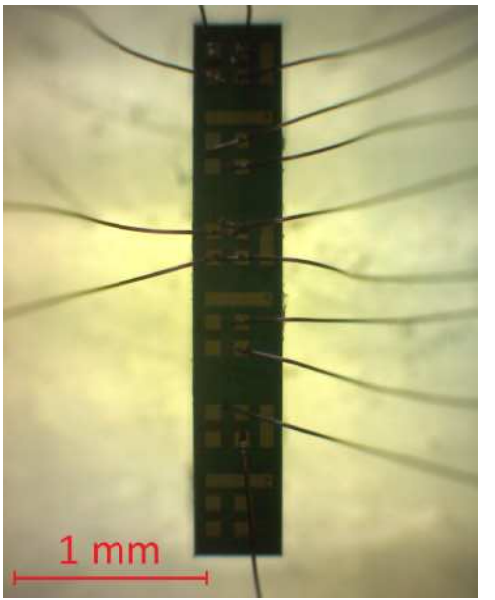


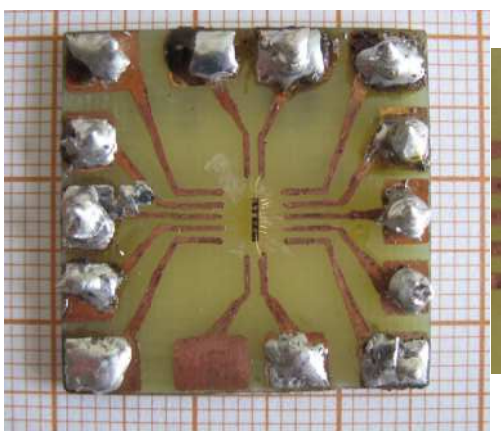
Nanowires of SbSI on Si/SiO_2 substrate with Au electrodes after ultrasonic welding

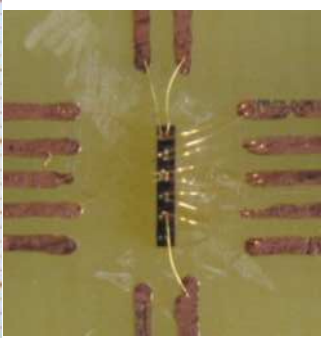


Ultrasonic bonding



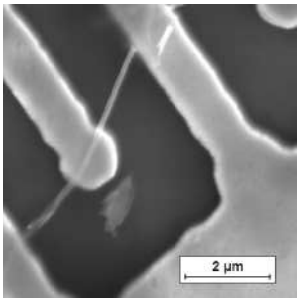


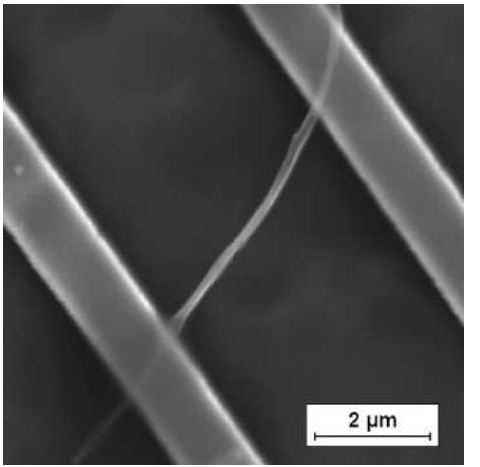


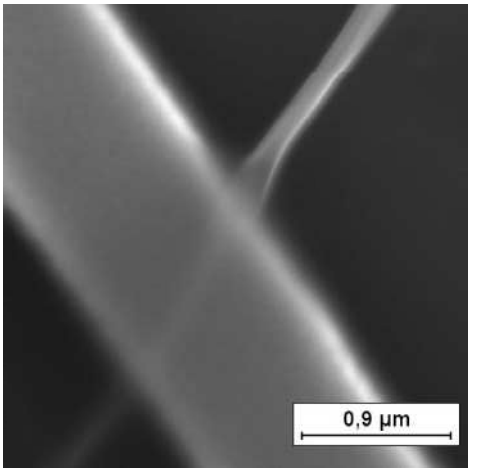


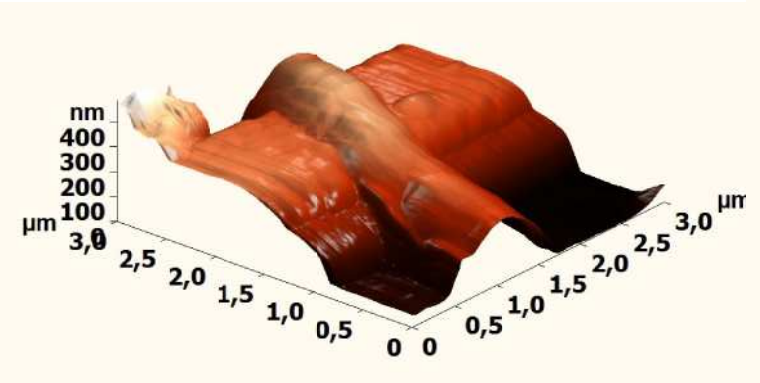
The electrical contacts made using wedge ultrasonic bonding.

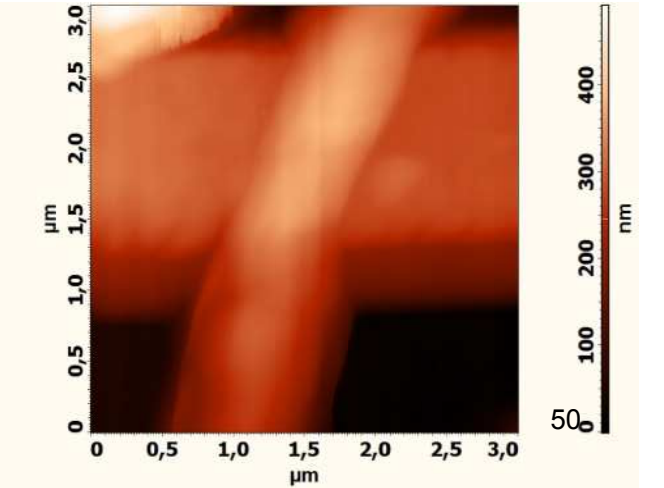
Carbon nanotubes on Si/SiO_2 substrate with Au electrodes after ultrasonic welding





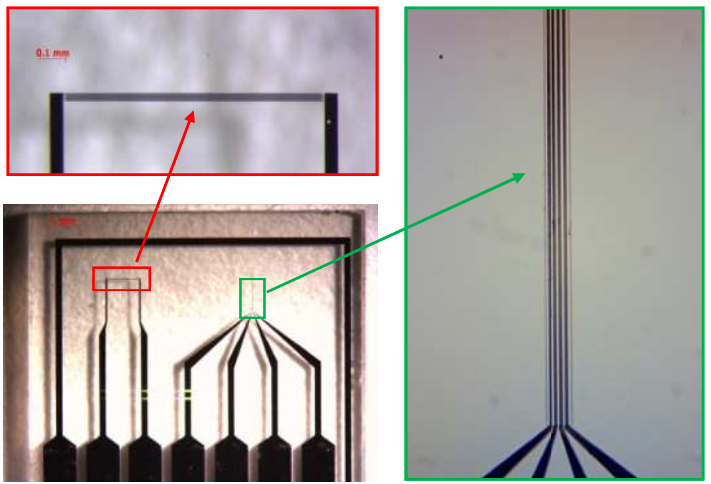


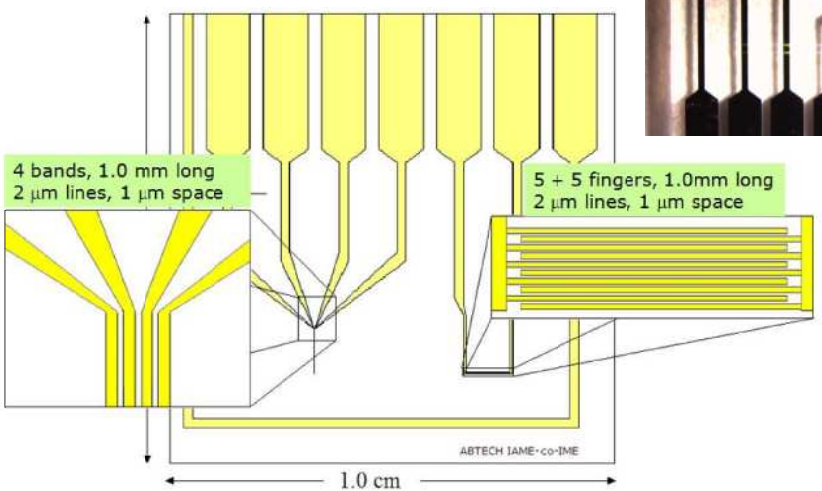


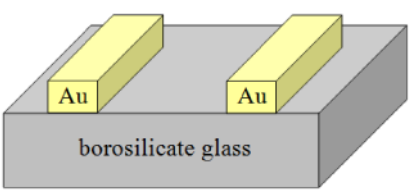


Glass Substrates

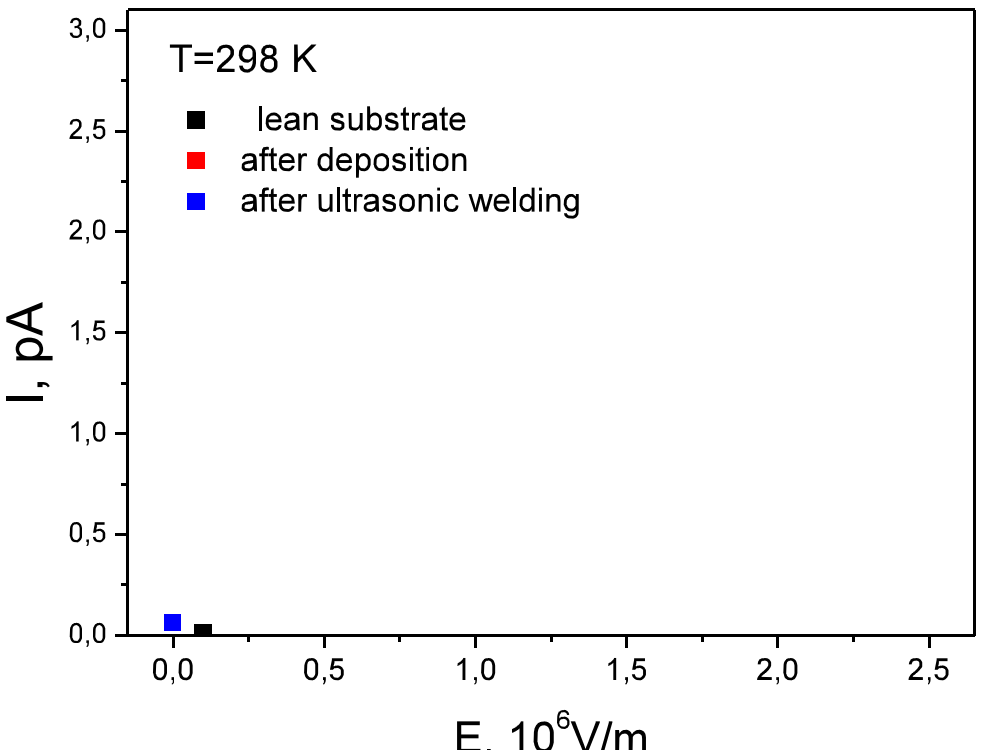
made by:
Abtech Scientific Inc.
electrode spacing: 1 μm



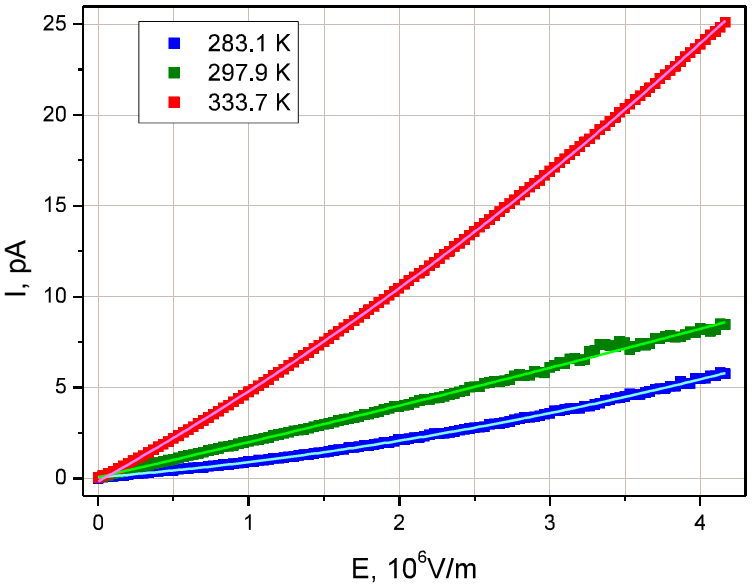




Nanowires of SbSI on glass substrate



DC electrical measurements



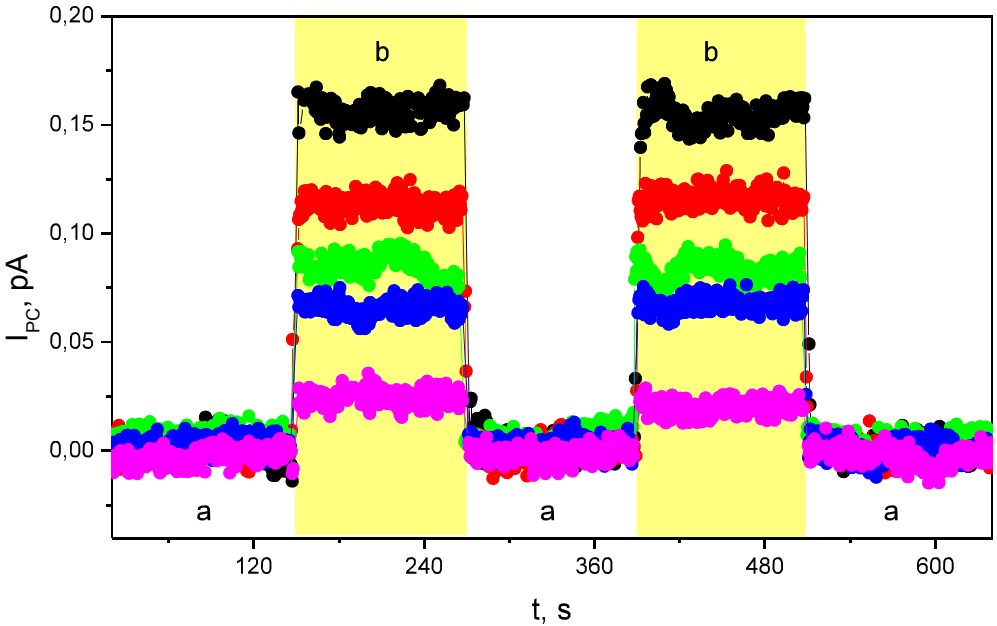
$$I = (A_0E + B_0) + C_0E^2 \quad [14]$$

ohmic conductivity — space charge

T, K	283.1	297.9	333.7
A_0, 10^{-18} S·m	0.662(10)	1.901(37)	4.607(14)
B_0, 10^{-14} A	5.20(91)	5.0(33)	-17.9(13)
C_0, 10^{-25} S·m²/V	1.717(23)	0.365(85)	3.574(33)

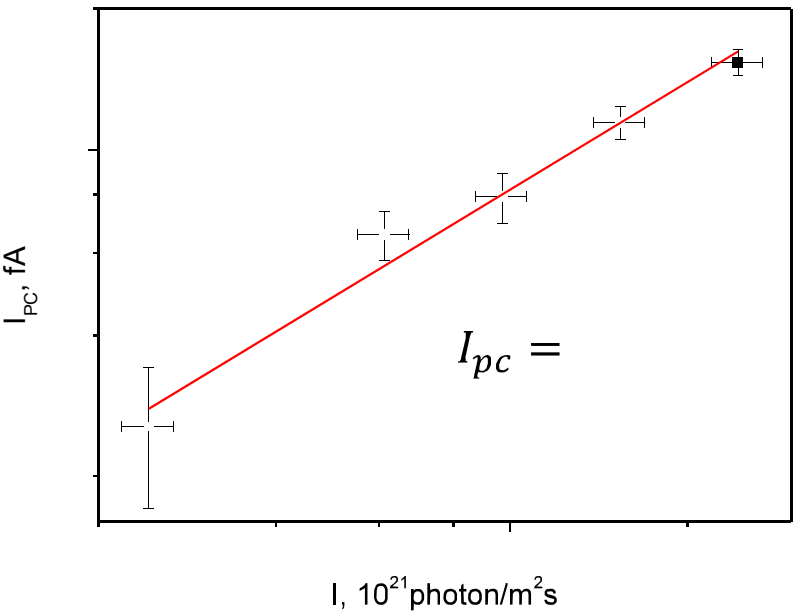
Current-voltage characteristics of SbSI single nanowires at different temperatures: ■ - *T*=283.1 K; ■ - *T*=297.9 K; ■ - *T*=333.7 K ; *p*=1.3(7)x10^{-5} mbar; —, —, — fitted curves.

Photoconductivity of SbSI nanowires



Kinetics of photocurrent in unilluminated (a) and illuminated (b) SbSI nanowire measured for different light intensities: ■ - 100% I_0, ■ - 63% I_0, ■ - 40% I_0, ■ - 25% I_0, ■ - 10% I_0 (λ=488 nm, I_0=2.4x10^{22} photon/(m^{2}s), E=2.0x10^6 V/m, T=298 K).

Photoconductivity of SbSI nanowires



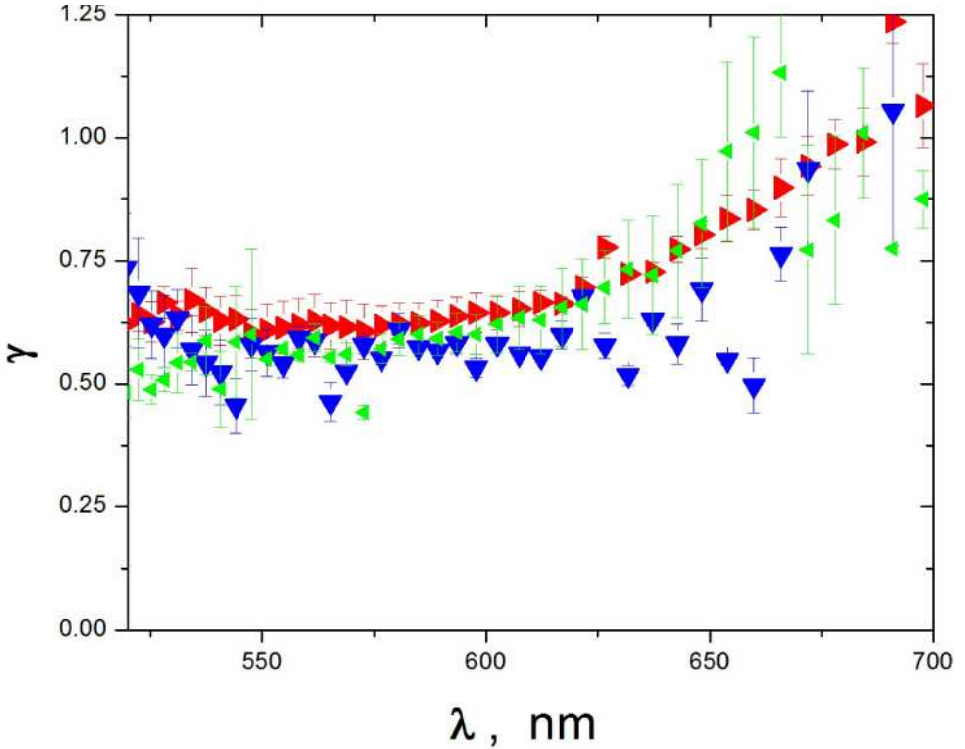
$\gamma =$

$\cdot \quad ^{-30}$ A

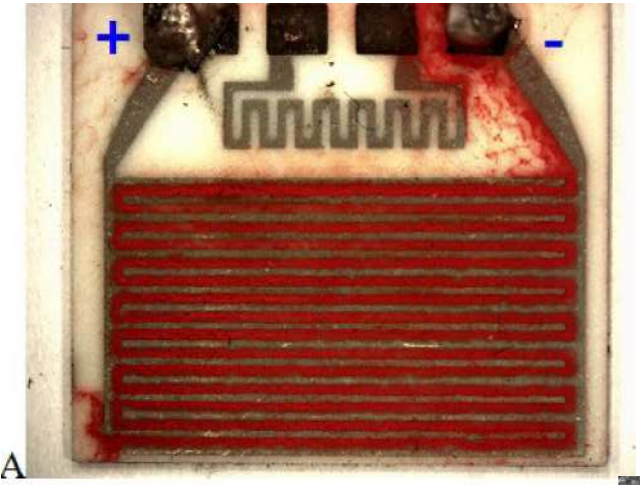
when: I_0 in photon/(m^{2}s)

Photocurrent as a function of light intensity (λ=488 nm, E=2.0x10^6 V/m, T=298 K).

$$I_{pc}(\lambda,T) = A(\lambda,T) I_0^{\gamma(\lambda,T)}$$

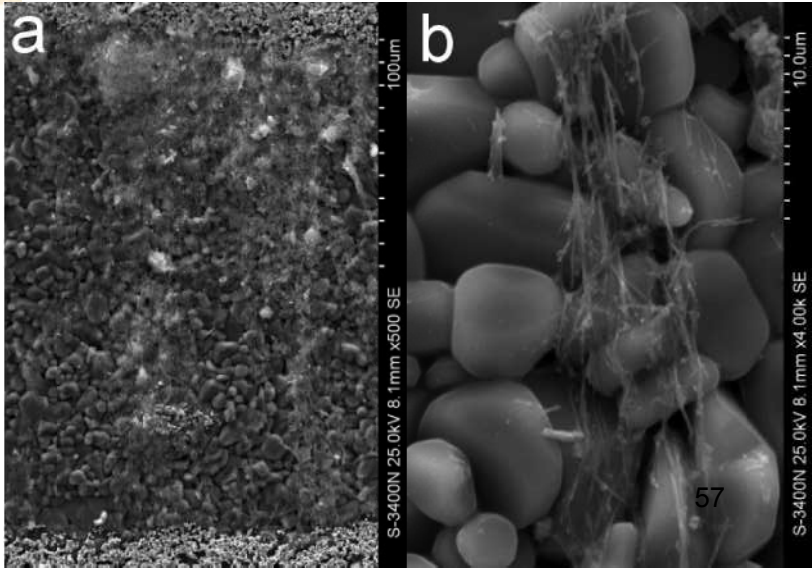


▼- 283 K, ◀- 303 K, ▼- 323 K

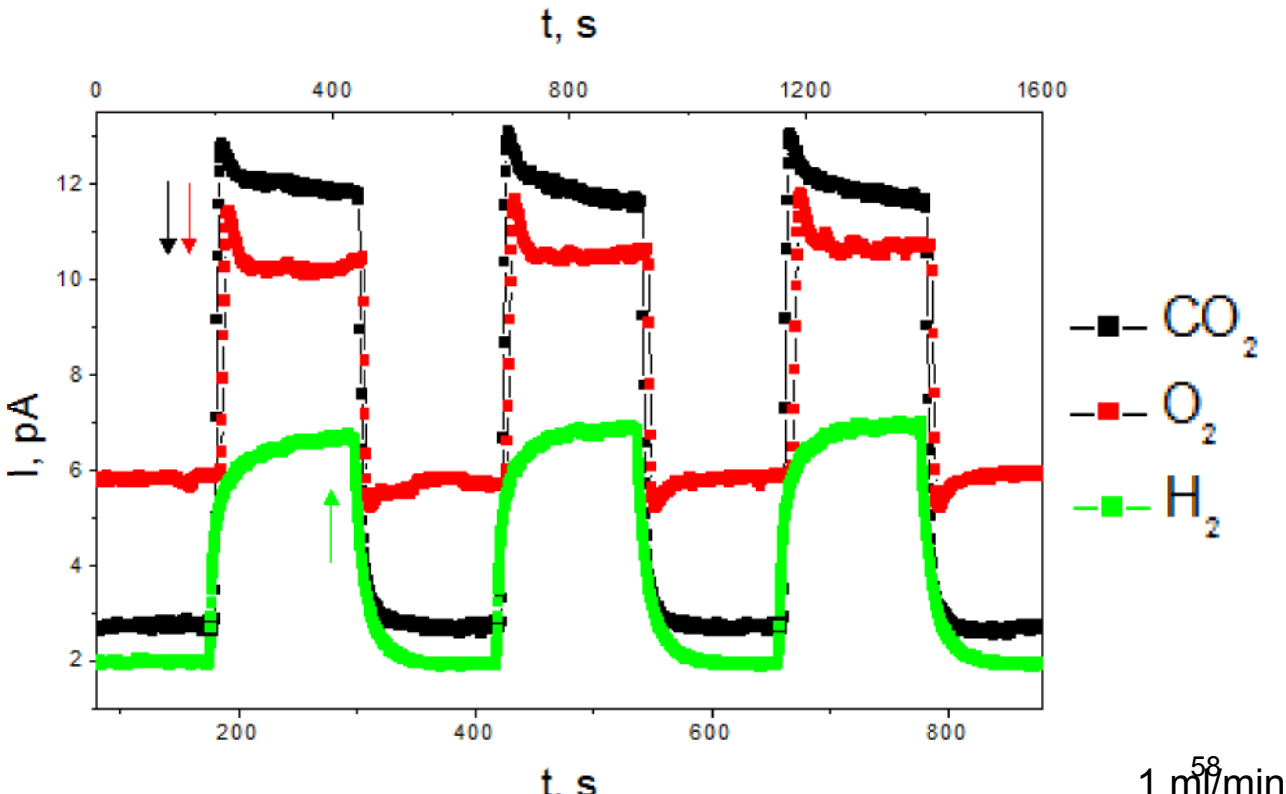


A 5 μm thick film of aligned SbSI nanowires on alumina substrate with interdigitated platinum lines as electrodes and the platinum temperature detector (· ^{5} V/m)

Low density of alligned SbSI nanowires on Al_2O_3 substrate
(· ^{5} V/m)

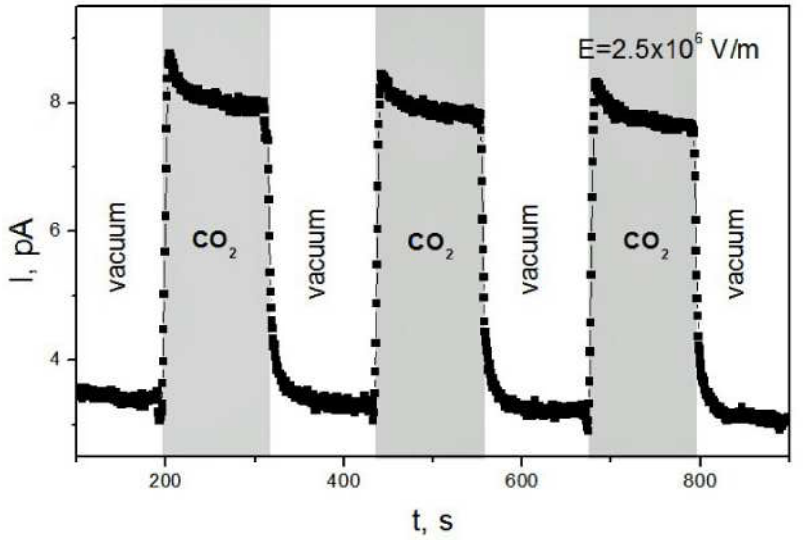


Nanowires of SbSI nanowelded to electrodes on glass substrate

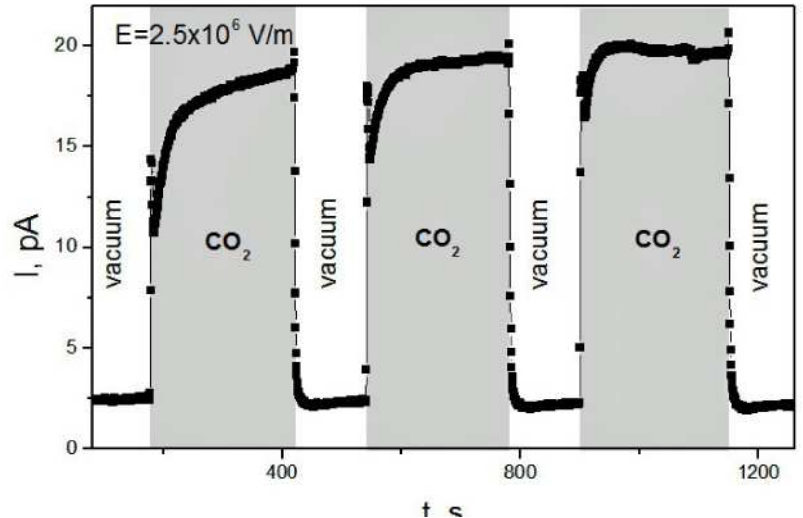


1 ml/min

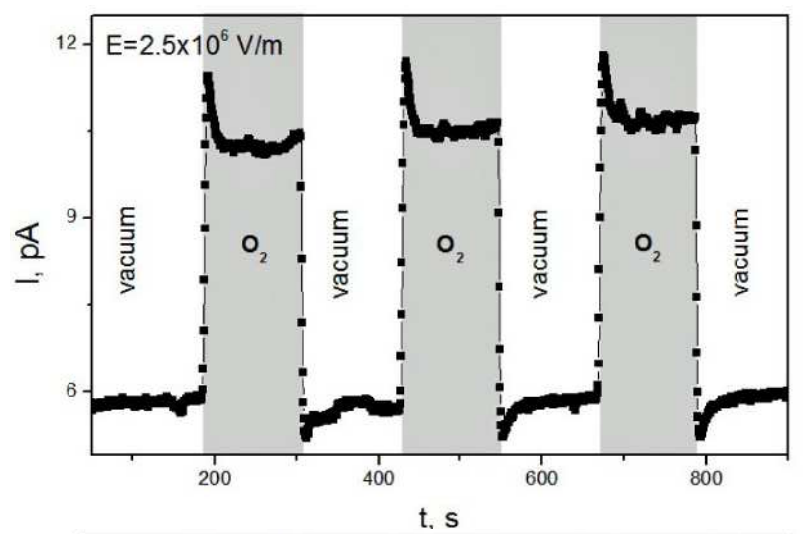
SbSI nanowires nanowelded to electrodes on glass substrate



0.5 ml/min

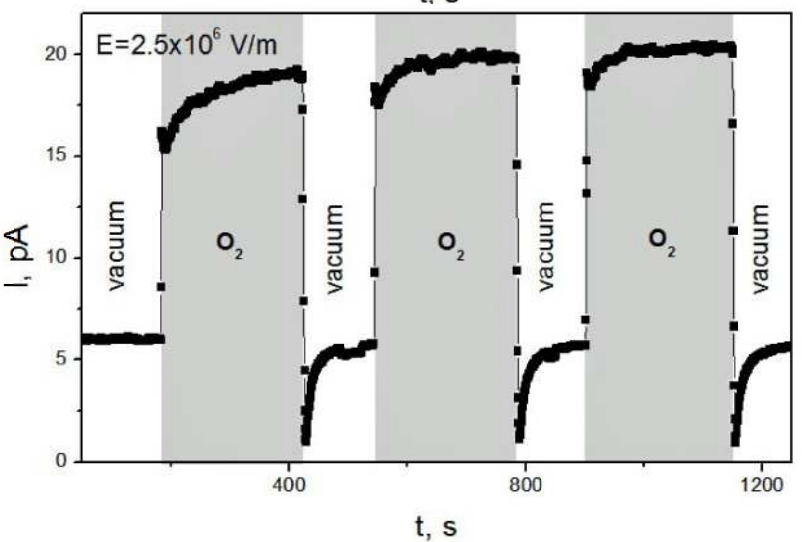


4 ml/min



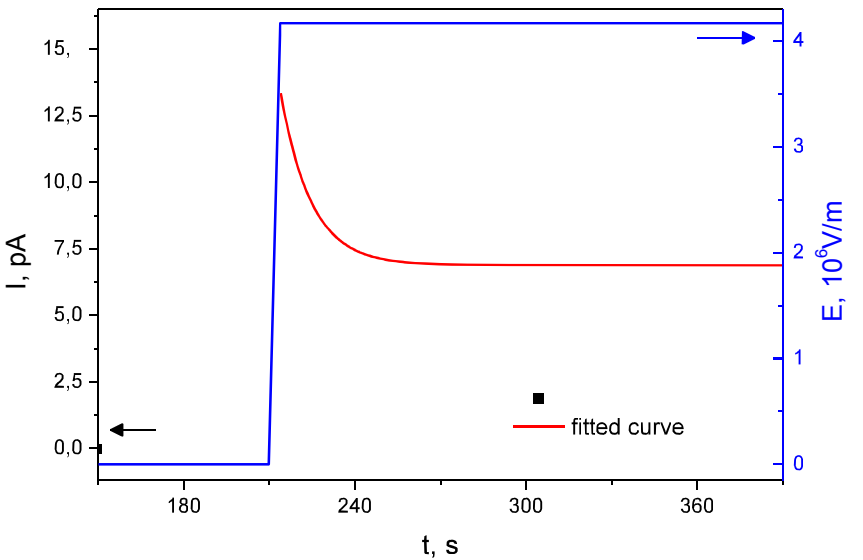
SbSI nanowires nanowelded to electrodes on glass substrate

1 ml/min



5 ml/min

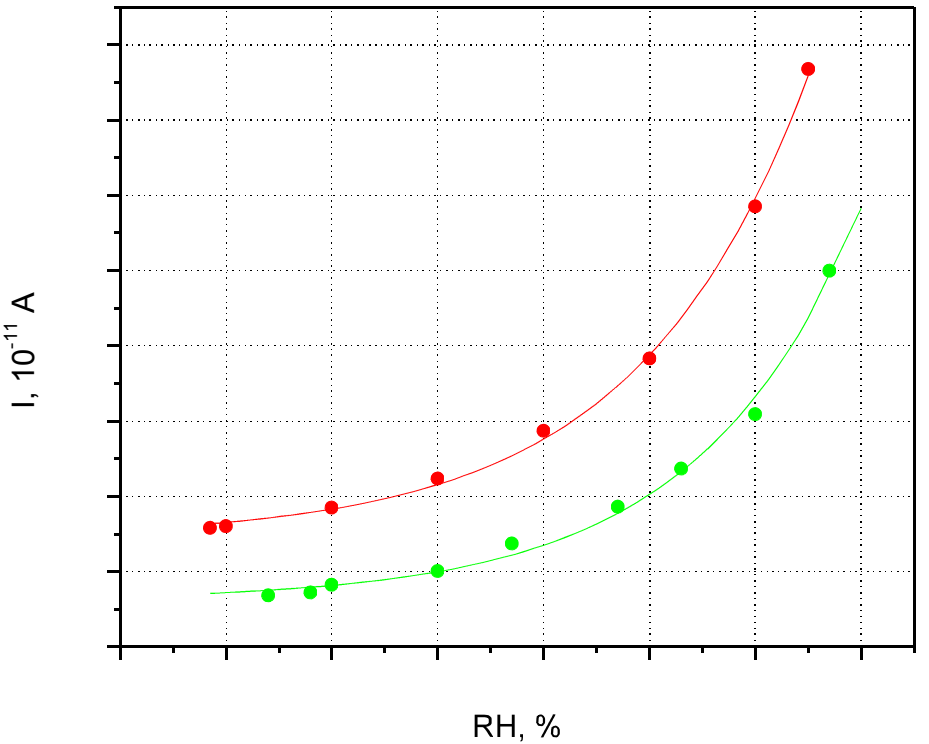
DC electrical measurements



$$I(t) = I_0 e^{-\frac{t}{\tau}} + I_{dc}$$

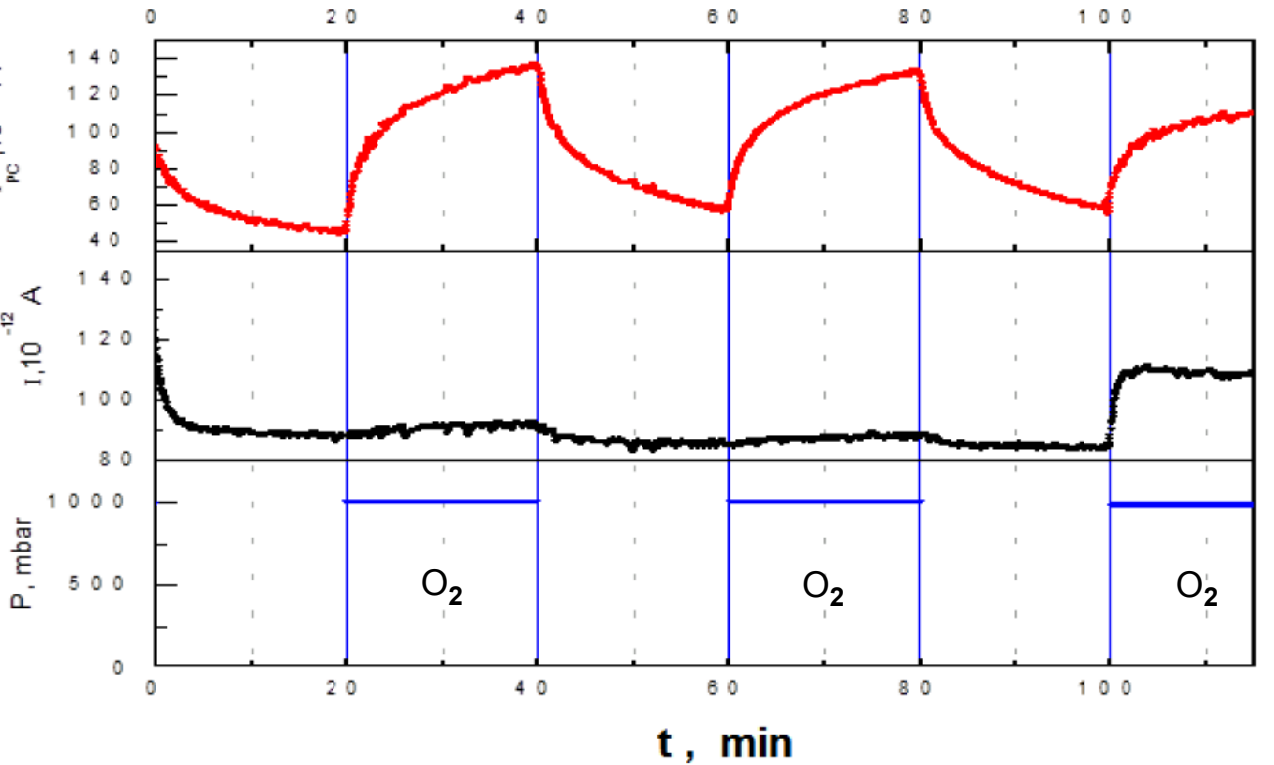
τ, s	10.74(28)
I_0, mA	2.9(15)
I_{dc}, pA	6.879(16)

Time dependence of applied electric field (E) and current response (I) measured for SbSI single nanowires (p=1.2x10^{-5} mbar, T=298.4 K).

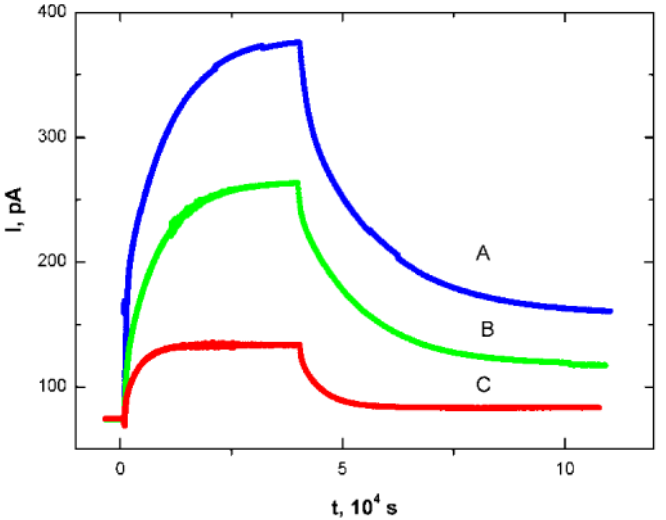


Current vs. relative humidity in the case of alligned no welded SbSI nanowires

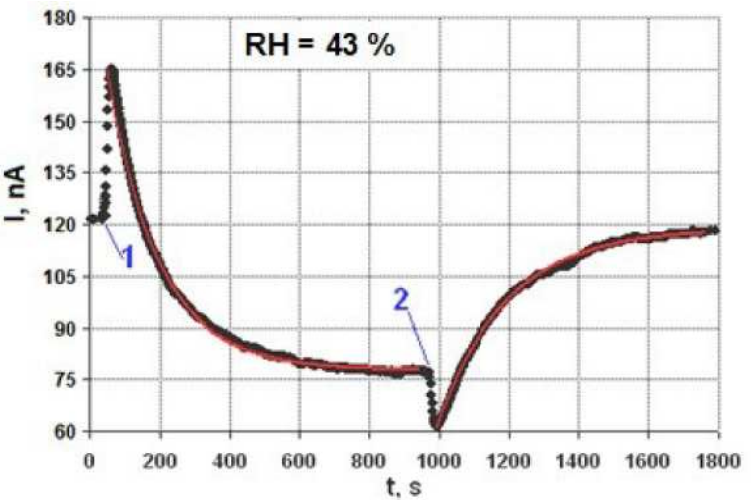
(λ=465 nm; I_0= · ^{19} photon/(m^{2}s); T = 280 K; T = 303 K)



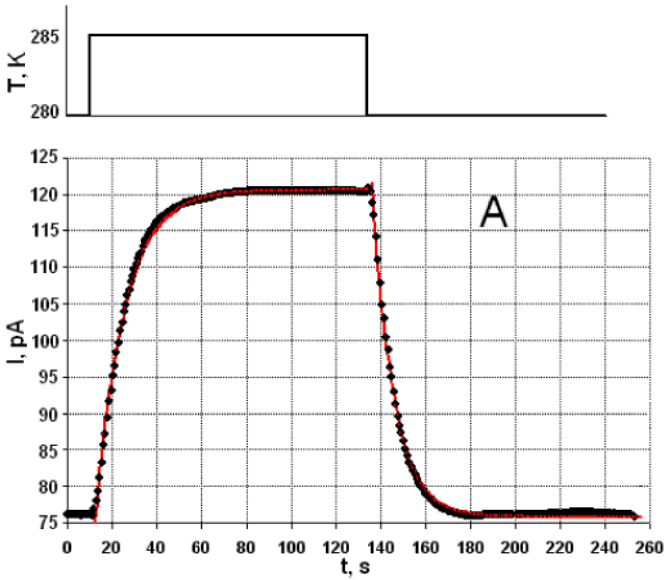
Kinetics of photocurrent in alligned no welded SbSI nanowires (λ=465 nm; I_0= · ^{19} photon/(m^{2}s); T=303 K)

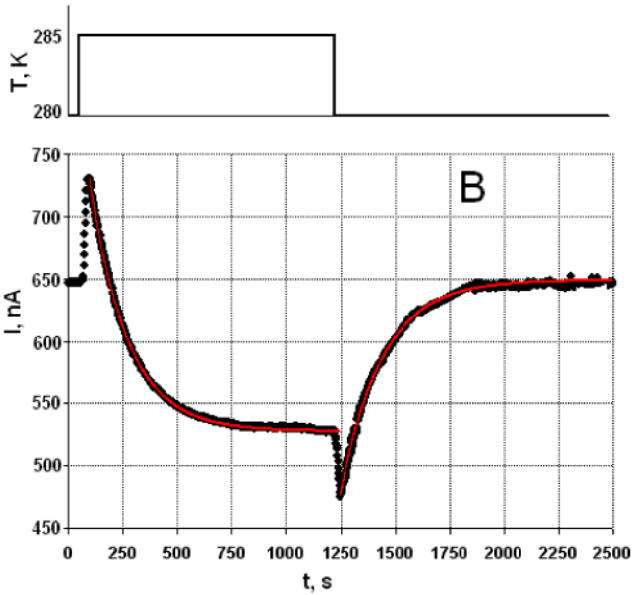


Kinetics of photocurrent in no welded SbSI xerogel in vacuum
(A- λ=465 nm; B- λ=518 nm;
C= λ=660 nm; p=1.1 mbar; T=288 K;
I_0= · ^{19} photon/(m^{2}s))



Influence of humidity on kinetics of photocurrent in SbSI xerogel in N_2
(λ=488 nm; I_0= · ^{21} photon/(m^{2}s))





Influence of temperature on electric current in SbSI xerogel in different environment

A- vacuum, p=1.1 mbar;

B- moist N_2 , RH=78 % at T=285 K and p =987 mbar.

Directions of future investigations

- gas nanosensors constructed from single nanowires of SbSI and SbSI@CNTs

- photodetectors constructed from single nanowires of SbSI and SbSI@CNTs

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Thank you for your attention